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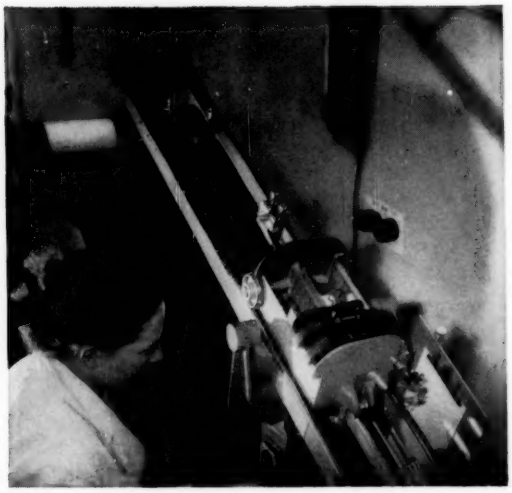

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Theory of Dyeing Polyester and Polyacrylic Fibers[1]

W. R. Remington and H. E. Schroeder

Jackson Laboratory,[2] Research Division, Organic Chemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

Abstract

These two fiber classes are similar in that both are dyed by disperse-type dyes; however, polyacrylic fibers can be dyed with anionic dyes if positive sites are provided. This can be done, for example, by using fiber containing ammonium groups. Alternatively, positive sites in the form of bound cuprous ions can be produced by treatment of the fiber with cuprous salts. In either case, ion exchange occurs in which colorless anions and dye anions compete for positive sites in the fiber.

In contrast, disperse dyes, which are used on all common fibers except cellulose and wool, require no specific dyeing sites. In polyethylene terephthalate, the dyeing reaction behaves like a simple solution in the fiber, with dipole interactions and dispersion forces probably very important.

The rate of dyeing of polyethylene terephthalate tends to be inconveniently slow, and organic compounds called carriers are used frequently to increase the rate. They are effective by increasing the diffusion rate of dye through the fiber.

THE very rapid growth of the synthetic fiber industry has demanded that practical dyeing processes for new fibers be developed as quickly as possible. In the case of the polyester and polyacrylic fibers, the development of practical dyeing processes was greatly expedited by the early development of an understanding of the physical-chemical fundamentals of dyeing reactions. As is so often true, the careful investigations of these dyeing mechanisms has led, in every case, to a picture of relatively simple chemistry. In this paper we shall attempt to summarize what is now known of the physical and chemical processes involved in the dyeing of polyester and polyacrylic fibers.

Most of this information is the result of work done in the Organic Chemicals and Textile Fibers Departments of the Du Pont Company. A great many men have made important contributions.

For several reasons the investigation of dyeing mechanisms and development of theories to explain the phenomena observed tend to be more exciting and rewarding in the field of synthetic fibers than in the field of natural fibers. One factor, as we have suggested, is the greater rate of change of the entire situation. Thus, the dyeing of the synthetic fibers has been much less completely worked out by empirical means so that there is more room for improvement and there has been less prejudice built up against changing methods. Also, the composition of a synthetic fiber is subject to control; when an investigation of dyeing mechanism indicates that a

[1] This paper was presented at the Perkin Centennial, Symposium on Theories of Dyeing, September 15, 1956, at the Waldorf Astoria, New York.

[2] Contribution No. 226 from Jackson Laboratory.

certain chemical or physical change could lead to a fiber with better dyeing characteristics, it is often possible to make the change. Furthermore, the student of the dyeing mechanisms for synthetic fibers has had at his disposal all of the knowledge which has been built up with regard to the dyeing of the natural fibers. For all these reasons the study of the dyeing mechanisms and development of theories for the dyeing of synthetic fibers has been very fruitful.

As we just mentioned, the chemical composition of the synthetic fibers is to a considerable extent controllable. As a result, when we work with a synthetic fiber, we can usually arrange to work with a material of very satisfactory chemical homogeneity. This means not only that one fiber is like the next, but also that within even a single fiber, variation of composition and physical structure is minimized. The man who studies the dyeing of a modern synthetic fiber need not be troubled by such complex features as the scales and cuticle of wool fiber, nor with degradative effects such as are caused by bacteria or fungi or sunshine during the growth of natural fibers.

Dr. Harris has already discussed the mechanism of dyeing polyamides with acid dyes, but it will serve as a useful introduction to the present topic for us to go over some of this ground again [1, 2]. Figure 1 is a schematic representation of a nylon fiber before and after dyeing with an acid dye. Only the end groups of the nylon polymer are shown because only they undergo a specific chemical change when the nylon is dyed. The dye anions and the protons from the dye bath are associated with the specific groups in the nylon, as indicated in the lower half of Figure 1. Expressed as a chemical equation

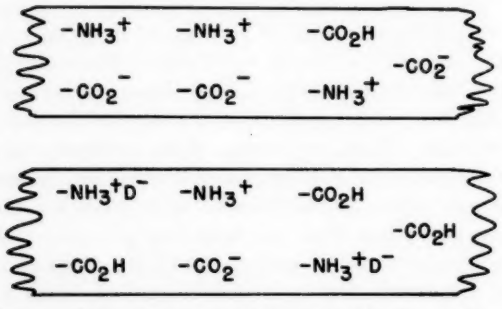

Fig. 1. Schematic representation of nylon fiber. Above, undyed; below, dyed.

(Equation 1), the dyeing reaction is quite simple.

$$D^- + H^+ + -NH_3^+ + -CO_2^- \rightleftarrows -NH_3^+D^- + -CO_2H \quad (1)$$

Where

D^- = Concentration of dye anions in bath

H^+ = Concentration of hydrogen ions in bath

$(-NH_3^+)$ = Concentration of undyed amino ends in fiber

$(-CO_2^-)$ = Concentration of undyed carboxylate ions in fiber

$(-NH_3^+D^-)$ = Concentration of dyed amino ends in fiber (abbreviated as D_F)

$(-CO_2H)$ = Concentration of carboxyl groups in fiber

The equilibrium constant for Equation 1 is

$$K = \frac{(D_F)(-CO_2H)}{(D^-)(H^+)(-NH_3^+)(-CO_2^-)} \quad (2)$$

For the purpose of testing the applicability of this equation, we rearrange it to give a straight line plot (Equation 3).

$$\sqrt{\frac{(D_F)(-COOH)}{(H^+)(D^-)}} = \sqrt{K}\,A - \sqrt{K}\,(D_F) \quad (3)$$

When the left side of this equation, represented as R, is plotted against the concentration of dye on the fiber, a straight line should result. Data obtained by equilibrating Metanil Yellow (Colour Index 138) with nylon were tested in this manner and yielded a straight line, as predicted (Figure 2).

As shown in Figure 3, two dyes (Quinizarine Blue, Colour Index No. 1073, and Metanil Yellow) applied to nylon simultaneously also yielded straight lines as predicted. This constituted an especially clear demonstration that anionic dyes compete for a limited number of sites in the nylon fiber.

The intercepts of the experimental lines in Figures 2 and 3 with the abscissa (A in Equation 3) are a measure of the concentration of dyeable sites—the amino groups in the fiber. This is a very precise method of determining the amine-end-group concentration in the fiber.

This information on the dyeing of nylon and wool was available at the time of early experimentation in the dyeing of polyacrylonitrile fibers. The poly-

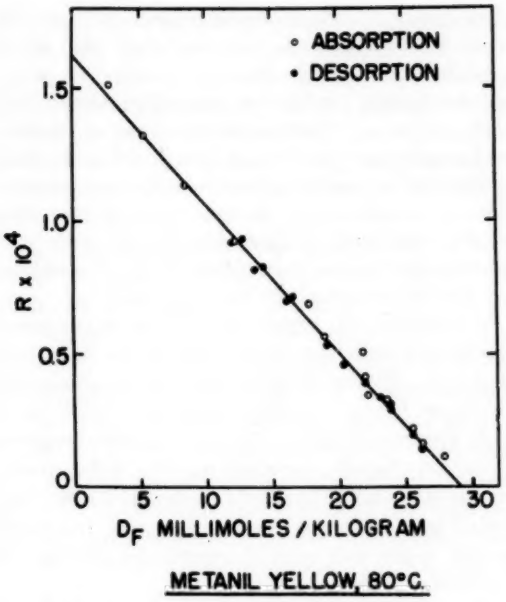

Fig. 2. Sorption of anionic dye by nylon.

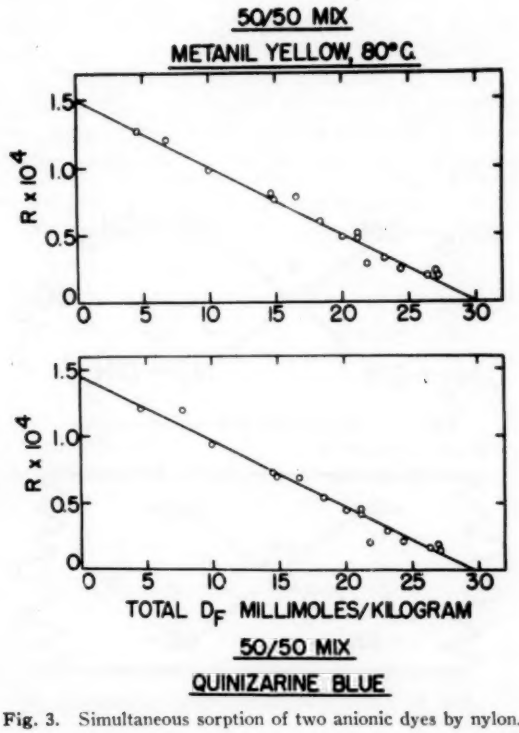

Fig. 3. Simultaneous sorption of two anionic dyes by nylon.

acrylonitrile fibers were very difficult to dye; they showed at *best* a very low affinity for any class of dyes. However, a simple, straightforward method of making these fibers dyeable with acid dyes appeared to be available in view of our knowledge of the mechanism whereby acid dyes combine with other fibers. Thus, the incorporation of basic dyeing sites for acid dyes was one of the earliest moves toward making polyacrylonitrile fiber more dyeable. This was done right in the reaction where the polymer was synthesized; an experimental fiber was made by copolymerizing acrylonitrile with about 6% by weight of vinyl pyridine, and the pyridine groups were expected to combine with protons to provide cationic sites for the sorption of anionic dyes (Figure 4).

A thorough investigation was made of the dyeing mechanism of this modified acrylic fiber, and the over-all picture agrees with our hypothesis, but the reaction is not quite as simple as was expected [3]. The data on the equilibrium dyeing of this fiber with an anionic dye, when plotted in a manner analogous to that used in assessing the data on nylon dyeing, did not yield the predicted straight line (Figure 5). However, when the amount of dye in the fiber is fairly large, the data do approximate a straight line.

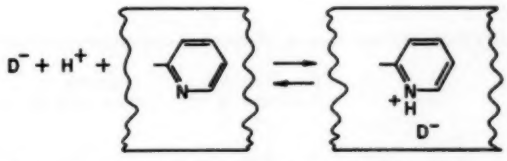

Fig. 4. Dyeing reaction for modified polyacrylonitrile fiber.

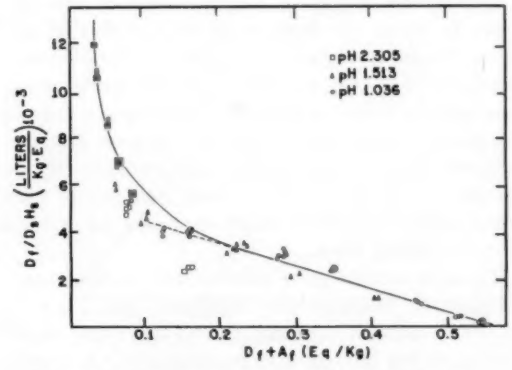

Fig. 5. Sorption of anionic dye by modified polyacrylonitrile fiber.

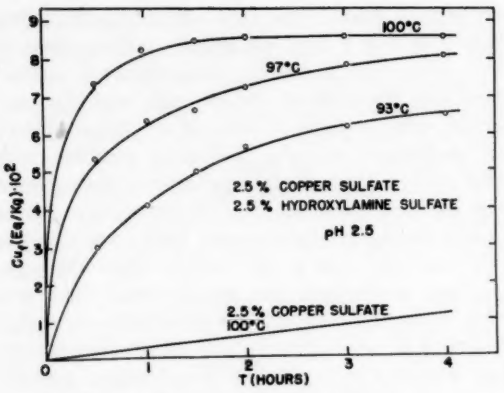

Fig. 6. Rate of sorption of copper by polyacrylonitrile fiber.

Actually, it is somewhat as though the fiber had a small reserve dye capacity which operated at all dyeing levels, but which we observed only when a relatively small amount of dye was in the fiber, which is where the data depart most seriously from linearity.

When the theory was modified so as to take into account the existence of two types of dyeing sites, it accounted for the data much more successfully. The curved line in Figure 5 is calculated in accordance with a two-site dyeing mechanism, the sites having the characteristics shown in Table I.

TABLE I. Dyeing Sites in Modified Polyacrylonitrile Fiber

Sites	Equil. constant, L^2/equiv. $\times 10^3$	Abundance, equiv./KG $\times 10^2$
Weak	7.9	56
Strong	770	3.1

The difference between the two types of sites appears to be in the basicity of the pyridine nuclei. Several reasons might be advanced for the difference in affinity of the two groups of pyridine nuclei; these may include interactions with neighboring groups in the individual polymer chains or between adjacent polymer chains. Some of the vinyl pyridine may be present as end groups, or sulfonic end groups may affect certain pyridine nuclei to make them more effective dyeing sites.

There is another more general way to make polyacrylonitrile fibers dyeable with acid dyes [3, 4, 5, 6]. This method does not depend upon any modification of the fiber as it is manufactured; it merely requires that the fiber contain a large number of nitrile groups. Dynel, for example, which is only about half acrylonitrile, was the first fiber to be dyed by this method—the only method we know of whereby one can dye an unmodified acrylic fiber with acid dyes. This involves treatment of the fiber with a metal ion, Cu^+, Ag^+, or Pt^{++}, which is absorbed by the fiber and makes it dyeable with colored anions. This procedure, using Cu^+ ion, of course, has been widely used in the dyeing industry and with very considerable success, even though it requires unusually careful control of the dyeing process.

In principal, the copper-dyeing process has much in common with the dyeing process we have just described. Figure 6 shows the rate of absorption of copper by an unmodified polyacrylonitrile fiber from aqueous solutions. The fiber absorbs cuprous copper very rapidly, especially near the boiling point. On the other hand, very little copper enters the fiber from a bath containing cupric copper, and this small amount might very well be cuprous by the time it penetrates the fiber.

These experiments show that cuprous ion has a specific affinity for polyacrylonitrile fibers, an affinity which is almost certainly related to the ability of cuprous ion to form complexes with nitriles, as was demonstrated 30 years ago [7].

Thus, the cuprous ion forms a complex with four molecules of acetonitrile (Figure 7). This complex tends to dissociate readily, and indeed cuprous ions are not strongly bound to acrylonitrile fibers, either.

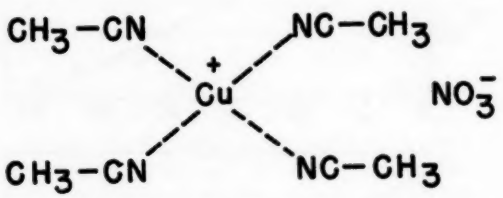

Fig. 7. Cuprous-acetonitrile-nitrate complex.

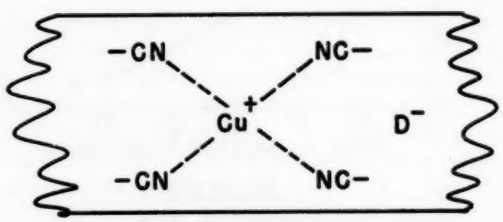

Fig. 8. Cuprous-polyacrylonitrile-dye complex.

They can be extracted by chloride or cyanide ions, which form complexes with the cuprous ions.

The mechanism by which the dye itself is bound to the fiber is relatively simple. Its negative charge neutralizes the positive charge on the cuprous ion. Just as the cuprous-acetonitrile compound contained a nitrate ion; so the cuprous-fiber complex will be associated with a dye anion (Figure 8).

In the discussion of copper dyeing, we have been speaking of acrylic fibers in general, but now we must take up a specific member of this group—Orlon acrylic fiber. Recently, in the dyeing of Orlon, anionic dyes have been largely supplanted by cationic (basic) dyes. Up until the time of their resurgence for this use, we had regarded the basic dyes as "has beens" for most textile uses. Now, however, they are very popular because of their excellent fastness, brilliance of shade, and ease of dyeing. Accordingly, we have studied the mechanism of their dyeing. Dr. A. W. Bauer, of Jackson Laboratory, plans to publish the details of this study in the near future.

Cationic dyes appear to dye Orlon by an ion exchange mechanism. The picture very much resembles the copper dyeing situation, except that the charges are reversed, and the ionic sites are already in the fiber. The active sites for dyeing seem to be acidic groups introduced during the polymerization. In the undyed fiber, these anionic sites appear to be associated with colorless positive ions. In the dyeing process, the colorless positive ions are displaced by the positively charged dye ions from the dye bath.

We have considered how polyacrylonitrile fibers can be dyed with cationic dyes and with anionic dyes. However, these fibers are unusually versatile in their dyeing behavior, and they can also be dyed with the un-ionized disperse dyes. Commercially, the disperse dyes are used extensively, but we know of no investigation of the mechanism of their attachment to acrylic fibers. However, it seems quite likely that they are absorbed by this fiber in much the same way as they are absorbed by other fibers, where the mechanism has been well elucidated.

The interaction of disperse dyes with Dacron polyester fiber has been thoroughly studied [8]. Most of the disperse dyes, as their name implies, do not dissolve easily in water, and furthermore many are complex mixtures which are quite difficult to purify. Both of these factors contribute heavily to the difficulty of studying their dyeing mechanisms.

In the studies which we shall describe, highly purified dyes were used, and their equilibrium distribution between Dacron fiber and *solution* in water was measured. The dyes were typical nonionic dyes, having the structures shown in Figure 9.

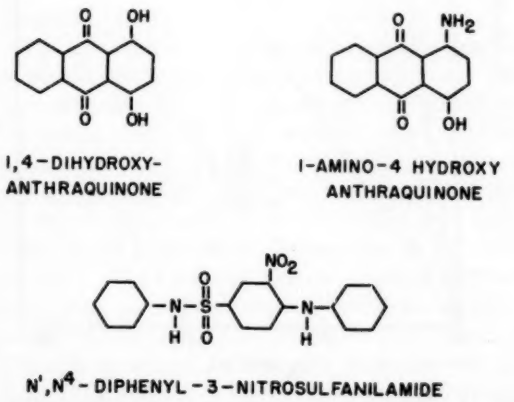

Fig. 9. Disperse dyes studied in Dacron polyester fiber.

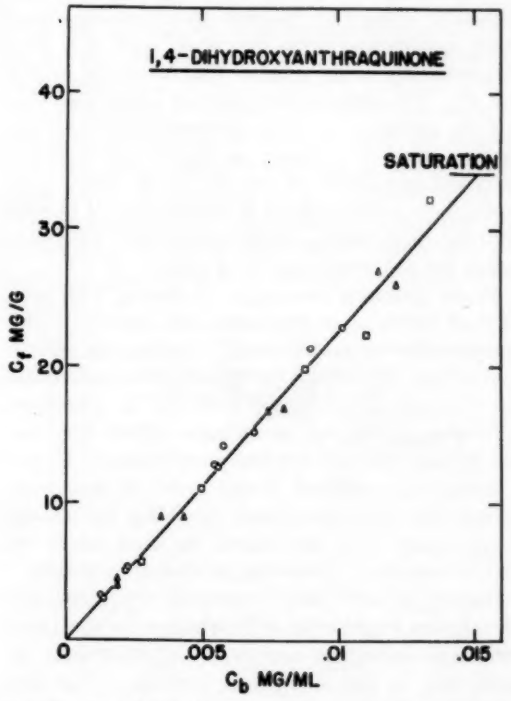

Fig. 10. Sorption of disperse dye by Dacron polyester fiber. △ Absorption; ○□ Desorption.

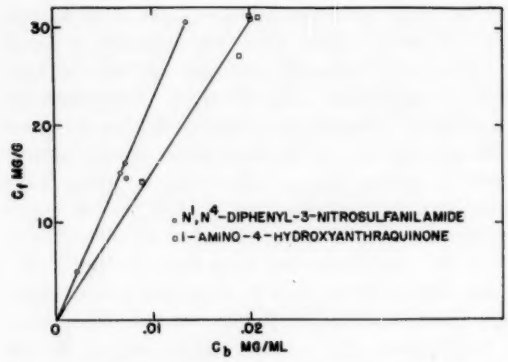

Fig. 11. Simultaneous sorption of two disperse dyes by Dacron polyester fiber.

When any of these dyes was equilibrated between Dacron polyester fiber and water at a series of concentrations, the data yielded a straight line. A typical plot is shown in Figure 10. The direct proportionality between the concentration of the dye in the water and the concentration of dye in the fiber holds up to the saturation point in both phases. Similarly, when two disperse dyes were simultaneously equilibrated with this fiber, each dye acted independently of the other. This is shown in Figure 11. The independent behavior of the two dyes and the straightness of the isotherms constitute convincing proof of a dyeing mechanism which is best described as solution of the dye in the fiber. Certainly there is no evidence of interference of one dye with the other, such as would occur if they were competing for a limited number of sites.

Under practical conditions of dyeing with mixtures of colors, some observers have reported a phenomenon known as "blocking," wherein one color is held off the fiber to a large extent. We believe that this is a rate effect caused primarily by significant differences in the rate of diffusion of the dyes into and through the polyethylene terephthalate. If such a dyeing is continued to the point of true equilibrium, the effect disappears, providing the amount of color used does not exceed the limit which the fiber is capable of dissolving at that temperature.

Dacron polyester fiber is partially crystalline, and the question might arise as to whether the dye penetrates the crystalline regions, or whether it is located only in the amorphous portions. Our best guess is that it will be located only in the amorphous portions, the regions where the fiber may be regarded as a supercooled liquid. If the dye does enter only the amorphous regions, the mechanism may truly be called one of solution, but not solid solution. As we understand it, a solid solution involves the presence of two or more substances in the same crystal lattice [9]. There is no evidence for this whatsoever. So we would not use the term "solid solution," and, indeed, we know of no dyeing mechanism where the term is applicable.

In Figure 12, we show how the saturation level of a rather typical dye for Dacron depends on temperature. The solubility of the dye in the fiber is strongly temperature-dependent, as would be expected, but let us consider what the saturation level might be at room temperature.

In Figure 13, the same data are put in more practical units and extrapolated to room temperature. It predicts that there will be relatively little dye dissolved in the fiber at room temperature at equilibrium, and that if more dye is put on at a higher temperature, it will tend to crystallize out on cooling to room temperature. Of course, dye does not exude

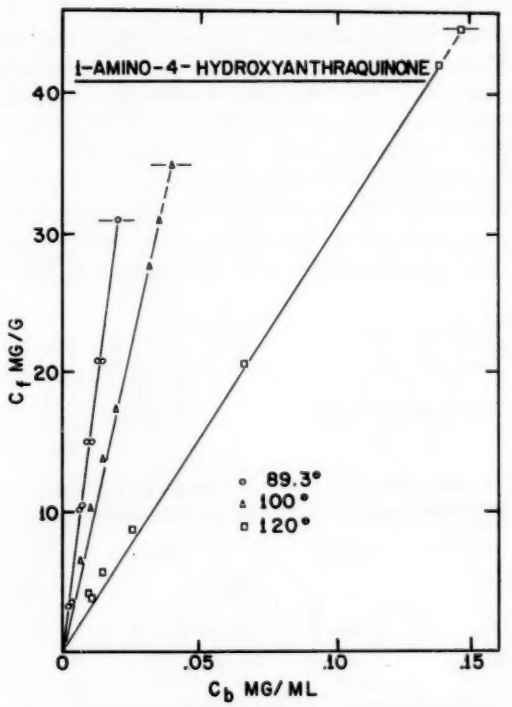

Fig. 12. Sorption of disperse dye by Dacron polyester fiber at three temperatures.

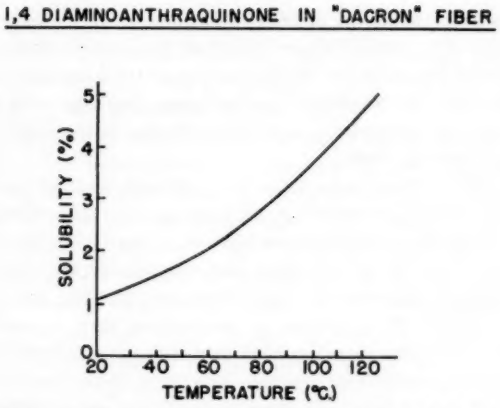

Fig. 13. Effect of temperature on solubility of disperse dye in Dacron polyester fiber.

from the fiber on cooling; what saves the situation is that dye molecules are almost entirely unable to move through the fiber at room temperature. Thus they stay where they are, and do not leave the fiber. The situation is analogous to that of trapped free radicals in polymers, where extremely reactive radicals may be preserved for long periods of time, simply because they cannot diffuse in the polymer [10].

Cellulose acetate is also dyed by disperse colors through the same mechanism by which they dye polyethylene terephthalate fibers. Our measurements, which have not yet been published, bear out this point very well, as is shown in Figure 14. Here we see the familiar linear dependence of equilibrium concentration of dye in the fiber on the concentration of dye in the water. Clearly, solution dyeing of the same type as for polyethylene terephthalate is involved [11].

Let us now turn our attention from consideration of equilibrium to the question of dyeing rates. The rate of dyeing, while an important consideration in the dyeing of natural fibers, became increasingly important with first nylon and then polyacrylic fibers, and became the matter of paramount concern in the dyeing of polyester fibers. In these fibers, especially, this problem goes right to the heart of the nature of the fiber. Their valuable physical properties depend upon high interchain forces to keep the polymer chains from slipping past each other. As a result, the polymer chains do not move aside very readily to let a dye molecule go past. Thus, the most serious limiting factor in the rate of dyeing both polyester and polyacrylic fibers is the rate of diffusion of the dye through the fiber. In particular, the rate of dyeing of polyester fibers at the boiling point of water is too slow to be practical. Nevertheless, these fibers are dyed commercially on a large scale with disperse dyes. The dyeing is made to proceed at a reasonable rate, either by operating at temperatures up to 120° C. under pressure [12] or by adding to the dye bath one of a group of compounds called "carriers" [13]. Carriers are colorless, aromatic compounds which have the effect of increasing the rate of dyeing of polyester fibers. On the basis of our most recent results, it appears that carriers operate by dissolving in the polyester fiber and, in effect, lubricating the interior of the fiber to permit more rapid diffusion of the dye molecules.

Full details of this study will be published by M. J. Schuler, of Jackson Laboratory, with whose permission we are using this material.

In an ingenious series of experiments, he showed that water itself is a powerful carrier. Furthermore, he showed that each of a large group of carriers of the customary sort (simple aromatic compounds) had essentially the same amount of carrier action, when the experiment was so arranged that each carrier was present in the fiber at the same molar concentration.

The remarkable similarity in the effectiveness of this group of carriers seems to support the conclusion that their mechanism of action is essentially independent of their structure. Apparently it is simply a loosening of the interchain forces permitting the polymer chains to move more readily and the dye molecules to diffuse through the fiber more rapidly.

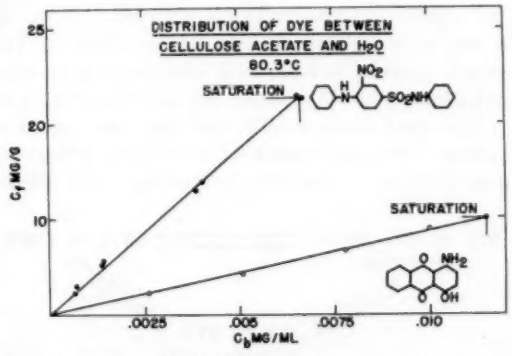

Fig. 14. Sorption of two disperse dyes by cellulose acetate (not simultaneous).

A sharp change in the freedom of movement of polymer chains is precisely what occurs at the glass transition temperature, and if, as we have proposed, carriers do enable the polymer chains to move about more freely, we should expect them to lower the glass transition temperature of the fiber. Actually, they do just that; they lower the glass transition temperature considerably.

Up to this point, we have described the nature of the phenomena which occur in dyeing with disperse dyes, and we have said a little about how fast the dyeing processes occur. However, there is another question which also deserves consideration, and that is why dyeing occurs when we put a fiber into a heated bath containing a disperse dye and wait, perhaps indefinitely. In Figure 15, we have indicated the phases in which the dye might be found. It might be that the equilibrium, to which we have referred so many times, would find the intended dye inside the fiber to only a very slight extent.

Since the dye of which we are speaking is of the disperse type, we shall assume there is no great problem with excess water solubility, but there may be a considerable problem with the dye's tending to remain in the solid state. For dyeing to occur, the forces tending to hold the dye molecule in the dye crystal must be overcome by those binding it in the fiber.

A study recently published by Majury has a definite bearing on this point. He has measured the absolute heat of dyeing of two simple disperse dyes for cellulose acetate [14]. That is, he has evaluated the heat which would be evolved if these dye molecules were to be transferred from the vapor state—where there are essentially no forces acting on them—to the interior of cellulose acetate. He has supplied an answer to the question: "How big is the force holding the dye in the fiber?" The answer is about 20 kcal./mole each for p-nitroaniline and azobenzene. These are not standard dyes such as are used commercially, but they are adequate models. The combination of azobenzene with cellulose triacetate is especially interesting. The affinity is as great as on ordinary diacetate. Since neither this dye, nor cellulose triacetate has any hydrogen atoms available for bonding, none of the heat of dyeing can be attributed to hydrogen bonding, which has been regarded as a principal factor in the affinity of disperse dyes.

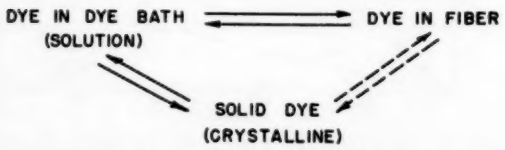

Fig. 15. Phases in disperse dyeing.

Thus, there appears to be a 20-kcal. heat of dyeing to be accounted for, without any hydrogen bond formation to attribute the heat to. Clearly, the binding must be of the same sort responsible for other solution phenomena where hydrogen bonding is not possible. By a process of elimination, then, it must be concluded that forces responsible for the binding of the azobenzene are the dispersion forces and dipole interactions. It appears likely that these forces would be the principal ones binding disperse dyes wherever they are used.

But in a real dyeing, we are not concerned with the dye in the vapor phase. The question of importance in a real dyeing is how the absolute heat of dyeing compares with the forces holding the dye molecule in the crystal. The crystal forces are the forces with which the heat of dyeing must compete. For all five of the dyes which he studied, Majury found that the forces holding the dye into the crystals almost exactly balanced the forces attracting the dye into the cellulose acetate. The heat effect accompanying transfer of dye from the crystalline form to the cellulose acetate ranged from 0 to 5 kcal. Interestingly, 4 kcal. is the value we found for the heat of dyeing Dacron polyester fiber with a disperse dye. Thus, in all of these cases, the reaction

$$\text{Dye (crystalline)} \rightarrow \text{dye in the fiber}$$

has a very small heat effect.

Clearly, the heat of reaction cannot be regarded as the driving force in this type of dyeing. We are then forced to conclude that the driving force must be the entropy increase which accompanies solution of the dye in the fiber. That is, the dyeing occurs because the dye is so much more disordered in the fiber than it is in the dye crystal.

Our theoretical picture, our fundamental understanding of how and why we are able to color polyester and polyacrylic fibers, is, as we have tried to indicate, highly developed, especially in view of the newness of these fibers. We believe that this understanding has facilitated development of the excellent practical techniques now used for dyeing these fibers.

Summary

Polyacrylonitrile fibers are dyed with anionic and cationic dyes, if sites are present. They can also be dyed with disperse or nonionic dyes.

Ionic dyes require sites. It has been found possible to provide sites through modification of the polyacrylonitrile, either in its preparation or after it has been converted to a fiber. Thus, copolymerization of acrylonitrile with vinyl pyridine affords basic groups which on protonation act as cationic sites for the dye anions. Equilibrium dyeing studies confirm this picture. In fibrous forms polyacrylonitrile can acquire cationic sites through treatment with cuprous salts which are believed to form complexes of the type $RCN \rightarrow Cu^{+}$ with cyano groups in the fiber. The fiber is then colored by an ion exchange reaction involving replacement of colorless anions by the more affinitive dye anions. A similar general picture for salt formation on anionic sites exists for absorption of dye cations.

In contrast, disperse dyes, which are used on all common fibers except cellulose and wool, require no specific dyeing sites. In the case of polyethylene terephthalate, a study of the equilibrium partition of pure dyes between the fiber and aqueous solution gave a straight line plot characteristic of a process of simple solution. The dyeing reaction therefore involves simple solution of dye in the fiber. In mixtures of dissimilar dyes, the individuals are absorbed independently as though the other compound was not present. Although the fiber cannot have specific sites for the dyes, there are probably significant dipole-dipole interactions between dye molecules and the polymer chains.

The rate of dyeing of polyethylene terephthalate tends to be inconveniently slow under ordinary dyeing conditions, but can be accelerated by increase in temperature or the use of organic compounds called carriers. These generally aromatic molecules are effective by increasing the diffusion rate of dye through the fiber. Their effect is shown to be independent of carrier structure but proportional to the number of moles of carrier dissolved in the fiber.

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The Steaming of Worsted Rovings[1]

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Introduction

Earlier studies in this laboratory have shown that the changes which occur in twistless assemblies of parallel wool fibers, such as top or French roving, on prolonged aging under constraint at normal temperature and humidity, are largely due to the relaxation of stress in the fibers [1]. A mild steaming treatment greatly accelerates the dimensional stabilization of the assemblies, and has a similar effect on their mechanical properties to that of prolonging aging. A small-scale spinning test indicated that steaming of freshly prepared roving improves the spinning efficiency [8].

These preliminary investigations left a number of questions unanswered, many of them sufficiently interesting to warrant an exhaustive study. Thus, it was felt desirable to establish the effect of steaming on spinning performance more definitely, to examine the effect of variations in steaming time and temperature, to study the penetration of steam into the roving package, and to extend the study to twisted ("Bradford") rovings.

Materials

The materials for the investigation were French tops prepared from three types of U.S.-grown wool —64's Rambouillet (R642), 60's Targhee (T602), and 56–58's Columbia (C562). All were from the 1952 clip of ewes from the flocks of the U.S. Sheep Experiment Station, U.S. Department of Agriculture, Dubois, Idaho, and were made available on loan to the Institute by the University of Idaho. (Some the preliminary work was performed on Targhee wool from the 1950 clip—T600). The fiber length data for these wools, in the grease wool, card sliver, and top stages, have been reported elsewhere [9]. The information for the top stage, together with data on the fiber diameter,[2] alkali solubility, and cystine content, are summarized in Table I.

TABLE I. Fiber Length and Diameter, Alkali Solubility, and Cystine Content of the Idaho Wools

		R642	T602	C562
Fiber length, single fiber tester, in.				
	Mean	2.56	2.80	2.60
	S.D.	1.19	1.26	1.35
Fiber diameter, μ				
ASTM method	Mean	22.5	25.1	27.7
	S.D.	4.7	5.3	6.5
Micronaire	Mean	22.4	24.5	28.3
Alkali solubility, %		8.8	7.3	7.3
Cystine content, Shinohara method, %		12.0	12.8	13.1

The three wools did not differ significantly in their fiber properties in single-cycle extension, measured at 65% R.H., 70° F.

Penetration of Steam into Roving Packages

The twistless rovings were prepared by conventional French drawing and were wound on wooden cores. The twisted rovings were made on a Saco-Lowell F5 rover and were thus on flangeless cardboard tubes; the prior drawing steps were performed on gilling and pin drafting equipment, 1½% oil, in the form of a 50:50 emulsion, being added at the first gilling.

Measurements of the temperature within the roving package were made by means of iron-constantan thermocouples inserted into the package. In the case of the French rovings, the thermocouples, with their leads enclosed in glass tubes, were pushed into the completed package; for the more compact twisted roving, the thermocouples were placed in the selected position in the package in the course of the roving operation. The steaming treatments were performed in conventional yarn steaming boxes, using the dry-bulb temperature as cycle starting control. The nominal relative humidity was 85% in all cases. The temperature within the box fluctuated ±5° F. around its nominal value.

[1] A report of work done under contract with the United States Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Western Utilization Research Branch of the Agricultural Research Service.

[2] Courtesy of W. von Bergen, Forstmann Woolen Company.

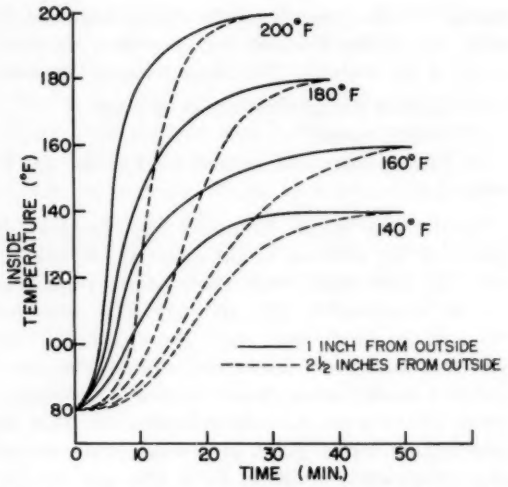

Fig. 1. The diffusion of heat into French Targhee roving bobbins at different temperatures.

In the experiments on French roving, the T600 wool was used. The thickness of the roving layer on the bobbin was $2\frac{1}{2}$ in. and its bulk density 0.36 g./cm.^{3}; thermocouples were inserted next to the core and at various distances, increasing at $\frac{1}{2}$-in. intervals, away from the core. Measurements were made on two bobbins, at different locations within the load, in each case. Location did not have a significant effect, and separate experiments indicated that the amount of wool present in the steaming box was also immaterial.

The smoothed time-temperature plots of Figure 1 show the results obtained at four temperatures for two positions on the bobbin, 1 in. from the outside, and $2\frac{1}{2}$ in. from the outside, i.e., at the core.

The time required to attain temperature equilibrium with the ambient atmosphere increases as the temperature is lowered, but even at the lowest temperatures used the process is complete within less than an hour. Separate experiments indicated that little change in the heat diffusion through the package resulted from perforating the bobbin core.

Temperature equilibration is very much slower at low humidity. This may be seen from the curves of Figure 2, which represent temperature measurements near the bobbin core, on packages with a $3\frac{1}{2}$-in. layer of roving, exposed to a temperature of 160° F. at 85% and 40% R.H., respectively. The initial regain of the roving was about 15%; the equilibrium regain at 160° F. and 40% R.H. is about 7%, and at 160° F. and 85% R.H., $16\frac{1}{2}$% [6]. Thus exposure to the former atmosphere will result in considerable moisture desorption, and to the latter in a small adsorption. The desorption is endothermic, and the low rate of heat penetration into the package at low R.H. is undoubtedly due largely to this factor; the lower heat capacity of the dried atmosphere will, of course, be a contributing factor.

The Bradford roving packages had a high bulk density (0.58 g./cm.^{3}) but the thickness of the wool layer was only $\frac{1}{2}$ in. Temperature equilibration was in this case very rapid, as indicated by the curves of Figure 3, which summarize the results of an experiment at 140° F. Ambient temperature is reached throughout the bobbin within 20 min., as against 45 min. for the French roving under the same conditions, and thereafter the whole of the package follows the temperature fluctuations of the ambient atmosphere very closely.

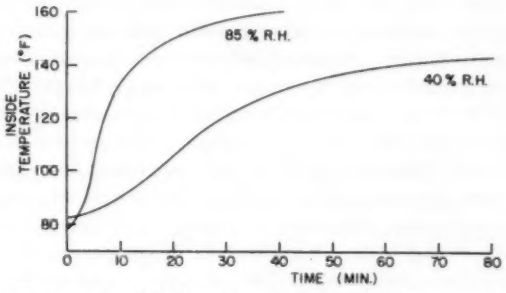

Fig. 2. The diffusion of heat into French Targhee roving bobbins at 160° F. and different relative humidities (thermocouples close to core, $3\frac{1}{2}$ in. from the outside).

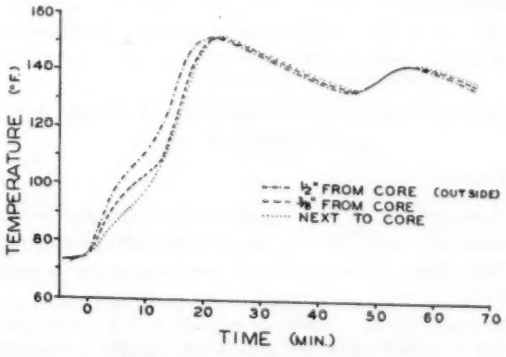

Fig. 3. The diffusion of heat into Bradford Targhee roving bobbins at 140° F. and 85% R.H.

Effect of Steaming Temperature on Spinning

In the first spinning trial, which was made on the French system, 50-lb. lots of 0.33 g./m. T600 rovings were spun on a McGlynn-Hays ring frame to 1/38's metric counts. Four lots were used, one being the control, and the others steamed at 160° F. for 1 hr., at 180°F. for 50 min., and at 200° F. for 40 min. The spinning took place between 24 and 72 hr. after the roving operation.

Like all the subsequent spinning trials, the experiment was laid out in a Latin square pattern, and the results were treated by variance analysis [3]. The mean end-breakage values obtained are recorded in Table II.

TABLE II. End Breakage in Spinning for Different Roving Steaming Temperatures

Steaming temperatures, °F.	No steaming	160	180	200
Ends down/1000 sp. hr.	135	106	132	152

The statistical significance of the difference between lots was low ($P = 0.1$ *); the trend is to improve spinning performance with lowering steaming temperature. A second series of tests was therefore performed, in which a range of counts (1/34's, 1/38's, 1/40's) was spun, and steaming temperatures of 140, 170, and 200° F. were applied. The results confirmed those of the first trial, indicating the optimum spinning performance for the lowest steaming temperature, and some worsening in spinning from the roving steamed at 200° F. in comparison with the untreated roving. 140° F. was judged the lowest practicable temperature to use, in view of the increase in time required for steam penetration into the package with lowering temperature; 140° F. at 85% R.H. for 1 hr. were therefore the conditions utilized in the comparisons of spinning performance of fresh, aged, and steamed roving discussed below.

Relative Spinning Performance of Fresh, Aged, and Steamed Rovings

French

In each of the French spinning trials, five lots of material, each 100 lb. in weight, were compared. Only three of these are of concern in the present study, but the presence of the others increased the total size of the test and thus improved the sensitivity of the analysis. The three relevant lots were:

1. Aged in roving for 4 weeks or more
2. Freshly roved
3. Freshly roved and steamed for 1 hr. at 140° F., 85% R.H.

In the case of the Columbia and Targhee, the whole of the drawing of the material for lots (2) and (3) took place immediately prior to spinning. In the Rambouillet, (2) and (3) were processed through the forefinisher stage along with (1) and stored in the form of forefinisher sliver. The counts for each quality were chosen to give an average of about 40 fibers per yarn cross section, i.e., near the practical limit spin. The processing details for the three trials are recorded in Table III.

TABLE III. Processing Details of the French Spinning Trials

	R642	T602	C562
Amount of roving per "treatment," lb.	100	90	100
Roving weight			
meters/g.	3.80	3.00	2.60
grex	2630	3330	3850
Singles counts			
metric	48	38	32
grex	208	263	313
Spinning twist, t.p.i.	14¼Z	13Z	12Z
Draft	12.7	12.6	12.3
Length of doff, hr.	7	5	4
Duration of test, spindle hr.	14000	10000	8000
Size of cell,* spindle hr.	280	200	160
Mean value of ends down per cell	63	49	45
Mean value of ends down per 1000 sp. hr.	226	243	281
Resting time of "aged" roving, weeks	5	15	5

* A cell contains a group of measurements representing pure replication, in this case one 40-spindle position in one doff.

The facing sides of two spinning frames were used; each frame side of 200 spindles was divided into five blocks of 40 spindles each. Each "treatment" occupied one block initially, the allocation being made at random, and was moved to a different block after each doff. For ease of handling, the movement of the treatments was systematized to one block to the right at a time. The experiment occupied five doffs, and the resultant pattern for each frame side was therefore a Latin square. The rea-

* P represents the probability of the null hypothesis, i.e., the probability of a difference as great as that found occurring by chance. Thus a P of 0.2 indicates that a difference as great as that observed would occur in one trial out of ten in the absence of any real effect.

sons for the choice of this design, and the factors involved in the analysis of the results, have been discussed in detail elsewhere [3].

The mean values of ends down/1000 spindle hours for each treatment obtained in the three experiments are recorded in Table IV. Two independent comparisons were made within each set—between the aged and steamed lots, and between the aged and steamed on one hand, and the freshly prepared roving on the other. The comparisons made are indicated in Table IV, and the resultant P values are recorded.

In none of the three cases was any significant difference in spinning performance noted between the aged and steamed lots. In two of the cases, there are indications that the aged and steamed rovings are superior to the freshly roved material, but the difference is small in magnitude and the statistical significance of the effect is low.

TABLE IV. French Spinning Trials. Summary of Results

Wool	Treatment	Ends down/ 1000 sp. hr.	P
R642	Fresh	251	
	Aged	249	Same*
	Steamed	238	Same*
T602	Fresh	303	
	Aged	240	0.05
	Steamed	261	Same*
C562	Fresh	347	
	Aged	317	0.2
	Steamed	310	Same*

* "Same" indicates $P > 0.2$.

TABLE V. Processing Details of Bradford Spinning Trials

	R642	T602	C562
Amount of roving per "treatment," lb.	90	33	83
Roving weight			
grains/yd.	2.57	3.18	4.00
grex	1820	2260	2835
Singles counts			
worsted	41.1	32.0	25.3
grex	215	277	350
Spinning twist, t.p.i.	16.2Z	13.0Z	12.1Z
Draft	8.5	8.2	8.1
Duration of test, spindle hr.	7800	1840	3600
Resting time of "aged" roving, weeks	4	4½	9½

Bradford

The processing details and quantities involved in the Bradford spinning tests are set out in Table V. Whitin Bradford ring frames were employed.

In all three trials, all the material was processed through the pin-drafter stages at the same time; the lots to be spun from freshly prepared roving were then stored in bags until required. The general pattern of the experiments was similar to that employed in the French trials, with some modification made necessary by the fact that small (48 spindles/side) frames were used. The results are summarized in Table VI.

The results indicate that the performance of both aged and steamed material is in every case superior to that of freshly prepared roving. The difference is both highly significant statistically and considerable in magnitude. In two of the three sets there are also smaller, but nevertheless appreciable, differences between the aged and steamed materials. These are not consistent (the steamed material spun better than the aged in the Rambouillet, and worse in the Columbia). It seems likely that these effects are due to variations in the preparation of the roving at different times; this complication does not arise in the steamed versus fresh comparison, since these two sets were processed together. The differences found are much greater than those observed in the French experiments; there is no doubt that twisted rovings are far more sensitive to "hot" spinning than twistless ones.

Mechanical Properties of Steamed Roving

In view of the effect which steaming has on spinning performance in twisted rovings, information is

TABLE VI. Bradford Spinning Trials. Summary of Results

Wool	Treatment	Ends down/ 1000 sp. hr.	P
R642	Fresh	456	
	Aged	314	0.001
	Steamed	172	0.01
T602	Fresh	168	
	Aged	104	0.01
	Steamed	108	Same
C562	Fresh	296	
	Aged	125	≪0.001
	Steamed	179	0.001

clearly desirable concerning its influence on the properties of the strand, and on those of the fibers composing it.

It is known that the properties of twistless strands, such as top or French roving, change on storage at normal humidity and temperature [1, 7]. Only a few data are available, however, concerning the effect of steaming [1]. With regard to twisted slivers, it has been shown that there is no appreciable change in the drag required to pull the strand apart in the absence of added oil [10]. No data appear to exist concerning the twist stability of such structures, or concerning the changes in the twist stability with aging or steaming. In order to obtain some information on these points, the following experiments were performed.

Single roving strands were extended to break on the Instron Tensile Tester at a 15-in. gauge length, using a constant rate of extension of 5 in./min., at 65% R.H., 70° F. In order to examine the twist stability of twisted roving, the tests were performed in two ways: (1) the strand was placed in the clamps immediately on removal from the bobbin, without allowing to untwist ("constrained"); and (2) the strand was suspended vertically, with its lower end free, for 2 min. before testing ("free"). The same procedure was adopted with the French rovings; in this case, while the effect of constraint was statistically significant (the values for stiffness and for breaking force being higher in the "free" tests), it was small in magnitude, and the changes in the properties with time ran in parallel in the two sets.

The steaming treatment was applied to freshly prepared rovings; the steaming conditions were 140° F., 85% R.H., 1 hr. Two roving bobbins were used per treatment; at each testing time, ten "free" and ten "constrained" tests were made per bobbin.

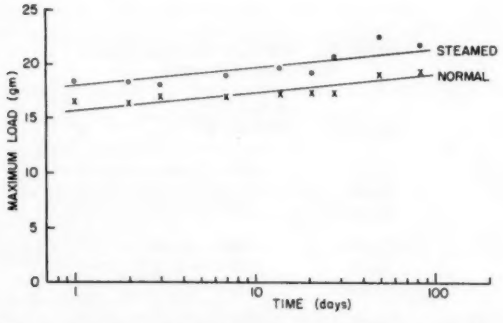

Fig. 4. The effect of aging on the breaking strength of French Targhee roving strands.

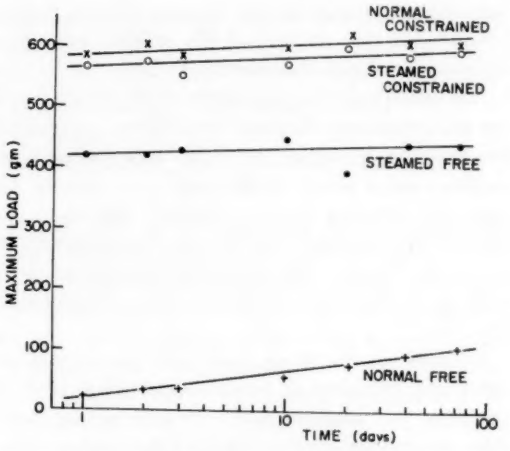

Fig. 5. The effect of aging on the breaking strength of Bradford Rambouillet roving strands.

The data for the breaking load of French Targhee roving are shown as a function of the logarithm of the time of aging on the bobbin at 65% R.H., 70° F, in Figure 4. The steaming has increased the breaking strength of the strand ($P = 0.1$); both steamed and unsteamed rovings increase in strength on aging ($P = 0.001$), the rate of increase being approximately linear with log time.

Corresponding data for Bradford Rambouillet roving are illustrated by Figure 5. There is no significant difference in the breaking load of unsteamed and steamed strands when tested in the constrained form; both exhibit a small increase on aging ($P = 0.01$). When freshly unsteamed roving is allowed to untwist for 2 min. prior to testing, its breaking strength drops to about the level found in French strands, whereas the steamed strand loses only about a quarter of its breaking strength. The unsteamed material gains in cohesion on aging, but even after 100 days it has achieved only a fraction of the breaking strength imparted by 1 hr. steaming at 140° F. The rate of strength increase appears linear with log time; extrapolation indicates that 10^6–10^8 days would be required to match the effect of steaming.

The differences in breaking strength are related (though nonlinearly) to twist stability, as shown by the data of Table VII, where the twist content and

TABLE VII. Twist Stability and Breaking Strength of T602 Bradford Roving, Aged 203 Days

Test condition	Twist, turns/10 in.		Maximum load, g.	
	Normal	Steamed	Normal	Steamed
Constrained	20.0	20.4	522	580
Free*	13.9	18.4	168	460

* After suspending free from constraint for 2 min.

breaking load of Bradford T602 roving, aged for 203 days, are reported.

The Properties of Fibers Exposed to Steam

Earlier experiments [2] in which the stress-strain properties of fibers from worsted yarn, before and after steaming at 180° F. had been measured, had revealed no significant changes resulting from the steaming treatment. At that time the low-strain (uncrimping) portion of the force-extension curve had not been studied; further experiments were therefore carried out to provide information on this point.

Newly spun French 1/38's metric yarn, from T602 wool, was used; three bobbins were steamed at 180° F. for 20 min., and 50 fibers were taken from them for testing, together with another group from three unsteamed bobbins as control. The fibers were vibroscoped to determine their cross-sectional area [4], and their force-extension curves were then determined on the Instron Tensile Tester at 65% R.H., 70° F. Each fiber was first stretched through the Hookean slope region of its force-extension curve, at a rate of strain of 10%/min., and immediately retracted at the same rate; after an overnight rest, it was extended to break at a rate of 50%/min. [2]. The uncrimping parameters and the elastic modulus were derived from the first extension, and the remaining data from the second. The results are summarized in Table VIII. It is evident that any changes in stress-strain properties resulting from the steaming treatment are slight.

TABLE VIII. Stress-Strain Properties of T602 Fibers from Unsteamed and Steamed Yarn

Property	Unsteamed	Steamed	95% Limits	P*
Uncrimping stress, megagrams/cm.²	0.107	0.084	±0.036	—
Uncrimping length, %	1.5	1.6	±0.1	—
Elastic modulus, megagrams/cm.²	30.7	30.4	±1.2	—
Stress at 5% extension, megagrams/cm.²	0.89	0.89	±0.20	—
Stress at 20% extension, megagrams/cm.²	1.098	1.084	±0.014	0.2
Stress at break, megagrams/cm.²	1.34	1.39	±0.07	—
Extension to break, %	29.6	33.1	±2.7	0.1

* Values greater than 0.2 not listed.

In view of the microscopically visible changes in the fiber surface known to be produced by mechanical processing and by exposure to steam [5], it was deemed desirable to examine the effect of steam on the frictional properties of the fibers. The device used for this purpose is shown diagrammatically in Figure 6. Two glass rods are mounted on the crosshead of the Instron Tester. The fiber is wound around them in the manner shown, its upper end being attached to the load-cell, and its lower end supporting a known weight (T_o). When the crosshead is moved downward, the tension registered by the load-cell (T_{RT} root-to-tip, or T_{TR} tip-to-root) consists of the force required to overcome the friction on the fiber and the supported weight.

With glass as the rubbing surface, the friction developed in the fiber on succeeding rubs rises over the first 2 to 3 cycles, and thereafter remains at a constant value. The procedure used was to rub each fiber first five times in the with-scale direction, using a tension T_o of 0.68 g. at a crosshead speed of 0.5 in./min., over a 1-in. distance; then to reverse the fiber and repeat the measurement in the anti-scale direction. The mean values of the force developed on cycles 5 and 10 were determined, and the coefficient of friction derived according to the equation

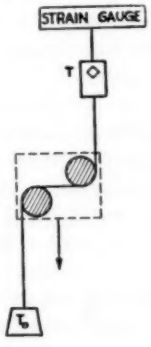

Fig. 6. Apparatus for measuring fiber friction.

$$\mu = \frac{1}{\pi} \ln \frac{T}{T_o}$$

The differential friction Δf was expressed as

$$\Delta f = \frac{\mu_{TR} - \mu_{RT}}{\mu_{RT}} = \frac{\mu_{TR}}{\mu_{RT}} - 1$$

The between-fiber variance in friction, as measured in the manner described, is large; the effect of steaming was therefore determined by retesting previously calibrated fibers. Twenty fibers taken from T602 aged French roving were tested; ten of these were then exposed to steam at 140° F., 85% R.H., for 45 min. After resting for a week at 65% R.H., 70° F., all 20 fibers were retested. The results are summarized in Table IX.

TABLE IX. The Effect of Steaming and Aging on Fiber Frictional Properties

Initial state			After 1 week		
μ_{TR}	μ_{RT}	Δf	μ_{TR}	μ_{RT}	Δf
			Aged and steamed		
0.52	0.47	0.10	0.55	0.49	0.14
			Aged only		
0.53	0.48	0.12	0.57	0.50	0.14

Both sets of fibers show an increase in friction and an increase in the directional effect in the second test ($P = 0.05$). There is no significant difference between the steamed and unsteamed samples.

Summary

The penetration of steam into roving packages is quite rapid; even in the least favorable case examined, French roving at 140° F., temperature equilibrium is attained within an hour. The diffusion of heat is very much slower in a dry atmosphere than in the presence of steam.

The effect of aging or steaming on the spinning behavior of twistless rovings is slight. The performance of twisted rovings at the limit of spin is, on the other hand, substantially improved by several weeks of conventional aging or by a short exposure to low-temperature steam. The steaming treatment necessary for this purpose may be readily carried out in conventional yarn-steaming equipment. It is therefore possible for individual textile mills to evaluate the applicability of such a treatment to their operation.

The mechanical properties of twistless roving are only slightly affected by steaming. Both normal and steamed French roving strands consolidate slightly with aging.

In Bradford rovings exposure to steam results in a high degree of twist stabilization; steaming is much more effective in this respect than conventional aging. In consequence, steamed roving loses much less of its twist than unsteamed roving when allowed to hang free; and the mechanical properties of the two strands, tested in the "free" form, are radically different.

Exposure to steam under the conditions employed in these experiments has no detectable effect on the stress-strain properties of the fibers, or on their surface frictional behavior.

Acknowledgments

The author is indebted to Dr. J. H. Wakelin and Dr. H. P. Lundgren for much helpful discussion; to Dr. J. H. Dusenbury for the supervision of the preliminary steaming experiments; to the Forstmann Woolen Company (Mr. W. von Bergen and Mr. C. Clutz) and to the American Viscose Corporation (Mr. R. L. Smith and Mr. W. Byers) for the provision of facilities and assistance for the processing tests; and to Mr. P. C. deMaCarty, Mrs. L. Templeton, and Miss E. Voong for assistance in the experimental work.

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The Crystallite Orientation in Different Varieties of Jute Fibers of Known Strength

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Abstract

The orientation of micelles in jute fiber of different varieties, both Tossa and White having different values of intrinsic strength and quality ratio, has been studied. The Hermans' orientation factor, average angle of orientation, and angle at 40% intensity of ten different samples of jute fibers have been determineed from the intensity distribution curves of the equatorial arcs, in the X-ray diffraction photograph. It has been observed that the orientation factor and angle at 40% intensity have no correlation with the intrinsic strength, but there is a slight correlation if the two varieties of jute White and Tossa are taken separately. For the same value of strength these two varieties have different values of orientation factor. The quality ratio of the yarn has no correlation with the orientation factor and the angle at 40% intensity. It has been further observed that the average angle of orientation varies from 8° to 9° approximately in the case of jute fibers, and Hermans' orientation factor varies from 0.96 to 0.97, whereas those of ramie are 7°36′ and 0.973, respectively.

Introduction

In jute fibers the crystallites or the crystalline areas have a uniaxial orientation, i.e., the b axis of the crystallite makes small angle with the fiber axis, while the other crystal axes are randomly oriented about the fiber axis. The average angle of orientation is generally measured from the distribution of intensity of X-ray reflections along the arcs into which the diffraction spots are drawn out. The dependence of the physical properties of cotton such as tensile strength, luster, elasticity dyeing properties etc. on orientation have been investigated by many workers. Sisson [7], Berkeley and Woodyard [1] found correlation between the angle at 40% intensity and the strength for different varieties of cotton. Sirkar and Saha [6] determined the percentage of micelles oriented in directions making different angles with the fiber axis in the case of four different varieties of jute fibers of known strength, and by drawing curves with percentage of oriented micelles as ordinate and angle between the direction of orientation and the fiber axis as abscissa, they observed the height of mode of the curve to be larger in fibers of greater strength and it was not strictly proportional to strength. Sen and Woods [5] compared the half-maximum angle and Hermans' orientation factor of jute and ramie. They observed variation of the orientation factor for the tip, middle, and root of jute fibers, and the orientation factor for the middle portion of jute fibers was almost equal to that of ramie. They also observed a difference in the orientation factor of the two varieties of jute, Tossa and White.

The object of the present work is to study the influence of orientation of jute fibers on some of its physical properties, intrinsic strength, quality ratio for a large number of samples and also to study whether the two varieties of jute, Tossa and White, of same strength have different orientation of their crystallites around the fiber axis. The Hermans' orientation factor, average angle of orientation, and the angle at which the intensity falls to 40% of the maximum intensity were determined for ten different samples of jute fibers, both Tossa and White, having different known values of intrinsic strength and quality ratio. The samples studied were collected from the 1950–1951 crop harvested in the matured stage. The intrinsic strength or the substance strength of the fibers is obtained by dividing the breaking load of a filament by its linear density, and the quality ratio of the yarn is one hundred times the ratio of its breaking load in pounds to its grist (lb. per 14,400 yd.).

Experimental

The X-ray diffraction photographs of moderate intensity suitable for photometry were taken for all the samples. Nickel-filtered CuK radiation from a Hadding-type X-ray tube was used. The camera used was the same as used by Chowdhury [2].

Following Hermans' et al [3], a series of photometer curves of (002) and composite (101 and $10\bar{1}$) interferences were taken starting from the center of the diagram and proceeding along radial lines at angular intervals of 2°30′. In order to convert the density into intensity, one density log-intensity curve was drawn. This was determined experimentally by calibration. From these the intensity distribution curves as a function of the angular distance from the equator were drawn for both the Debye-Scherrer arcs of (002) and composite (101 and $10\bar{1}$) diffraction spots. These curves for all the samples studied are reproduced in Figures 1 to 10. The peak intensity in all the cases was taken as ten, an arbitrary unit. These intensity distribution curves represent the statistical spatial distribution of the paratropic planes of the crystallites in the fiber, and they may be designated by $I' = F'(\alpha_1)$ for (002) reflection and $I'' = F''(\alpha_2)$ for composite (101 and $10\bar{1}$) reflections, where α_1 and α_2 refer to the angular distance from the equator. The Her-

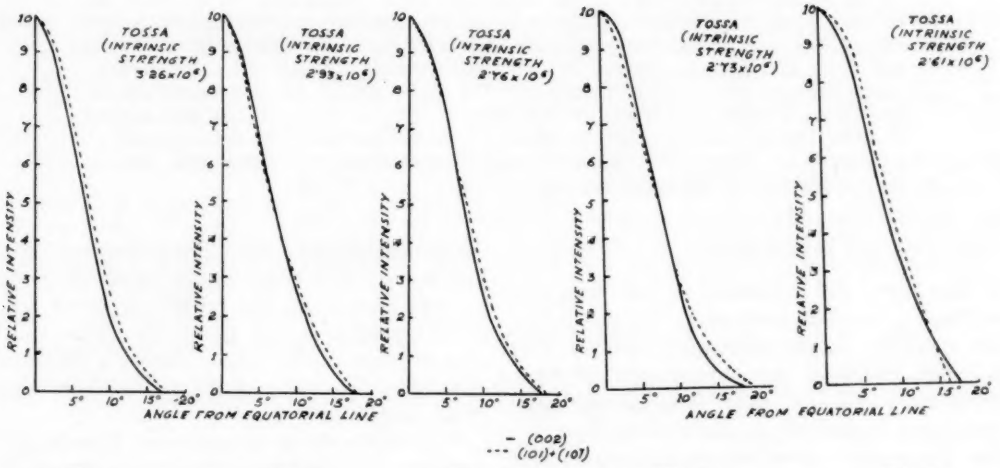

Fig. 1. Fig. 2. Fig. 3. Fig. 4. Fig. 5.

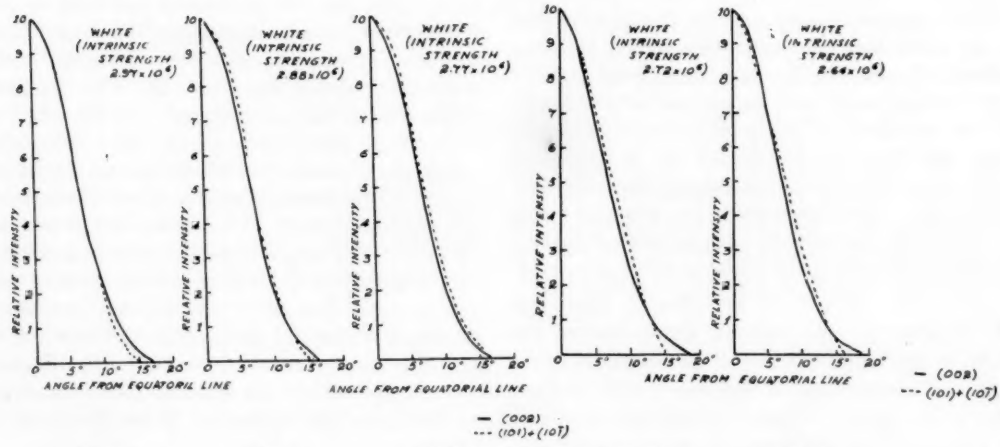

Fig. 6. Fig. 7. Fig. 8. Fig. 9. Fig. 10.

mans' average angle of orientation α_m and the Hermans' orientation factor f_x were found out from the following relations (Hermans [4]).

$$\sin^2 \alpha_m = \overline{\sin^2 \alpha_1} + \overline{\sin^2 \alpha_2}$$

and

$$f_x = 1 - \tfrac{3}{2}(\overline{\sin^2 \alpha_1} + \overline{\sin^2 \alpha_2})$$

where

$$\overline{\sin^2 \alpha_1} = \frac{\int_0^{\pi/2} F'(\alpha_1) \sin^2 \alpha_1 \cos \alpha_1 d\alpha_1}{\int_0^{\pi/2} I \cos \alpha_1 d\alpha_1}$$

$$\overline{\sin^2 \alpha_2} = \frac{\int_0^{\pi/2} F''(\alpha_2) \sin^2 \alpha_2 \cos \alpha_2 d\alpha_2}{\int_0^{\pi/2} I \cos \alpha_2 d\alpha_2}$$

The values of $\overline{\sin^2 \alpha_1}$ were determined from the empirical intensity curves obtained by plotting $I \sin^2 \alpha_1 \cos \alpha_1$, and $I \cos \alpha_1$ against the angular distances and finally by the usual method of graphical integration of both the curves and taking the ratio of the integrals. Similarly the values of $\overline{\sin^2 \alpha_2}$ were found out and hence f_x and α_m.

Results and Discussions

The values of f_x, α_m, and angle at 40% intensity in the intensity distribution curves of (002) reflection of all the samples with their intrinsic strength and quality ratio are given in Table I. The relation between the values of f_x and angle at 40% intensity for both the varieties of jute, Tossa and White, with the intrinsic strengths is shown graphically in Figures 11 and 12.

The results obtained as shown in Table I indicate practically no correlation between the intrinsic strength and the Hermans' orientation factor f_x or the angle at 40% intensity. But if the intrinsic strength of the two varieties of jute, Tossa and White, are correlated separately with the angle at 40% intensity and f_x as shown graphically in Figures 11 and 12, better correlation is observed.

TABLE I. Average Angle of Orientation, f_x, and Angle at 40% Intensity of All the Samples of Jute Fibers with Their Intrinsic Strength and Quality Ratios

No.	Variety	Intrinsic strength $\times 10^{-6}$	Quality Ratio	Angle at 40% intensity	Hermans' average angle α_m	f_x
1	Tossa	3.26	118.7	7°30′	7°57′	0.971
2	"	2.93	78.7	8°0′	8°44′	0.966
3	"	2.76	89.2	8°15′	8°43′	0.964
4	"	2.73	75.6	8°30′	9°3′	0.963
5	"	2.60	94.5	8°45′	9°12′	0.962
6	White	2.97	86.7	7°30′	7°54′	0.973
7	"	2.88	105.1	7°30′	7°51′	0.972
8	"	2.77	86.7	7°30′	7°58′	0.971
9	"	2.64	69.0	8°0′	8°20′	0.968
10	"	2.72	65.8	8°0′	8°26′	0.969

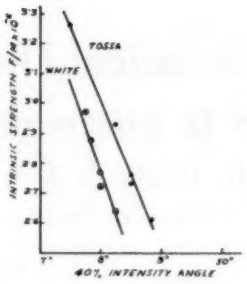

Fig. 11.

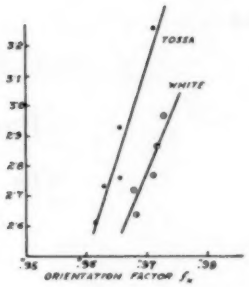

Fig. 12.

It is seen that there is a difference in the value of the orientation factor of the two varieties of jute, Tossa and White, of similar strength. The difference observed, however, is smaller than that observed by Sen and Woods [5].

It can be seen also from the table that no correlation exists between the quality ratios and values of f_x and angle at 40% intensity.

The average angle of orientation as seen from the table varies from 8° to 9° approximately in the case of jute fibers and f_x varies from 0.96 to 0.97, whereas (Hermans [4]) those of ramie are 7°36′ and 0.973, respectively.

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Chemical Damage in Wool

Part II: Effects of Alkaline Solutions[1]

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Abstract

The changes in the stress-strain properties of wet wool fibers upon exposure to solutions of varying alkalinities are reported. Cystine-lanthionine ratios found in these samples as interpreted from paper chromatograms are compared with changes in stress-strain properties. The presence of lanthionine in wool boiled in a solution at pH = 4.5 and in wool exposed to temperatures of 150° C. under atmospheric conditions is noted.

Introduction

That wool is readily damaged by alkaline solutions under certain conditions is well known. Such conditions are often suspected of being present in various processing steps during the manufacture of woolen fabrics. Scouring, steaming, dyeing, fulling, washing, and drying are all operations which may be carried out in an alkaline environment. Finished fabrics including papermakers' felts, compressive shrinkage blankets, Palmer blankets, and other industrial fabrics may encounter alkaline media. In spite of this, the extent of wool degradation under various alkaline conditions has not been well defined.

Alkaline damage in wool is characterized by conversion of cystine to lanthionine [15, 16, 18] with accompanying degradation of physical properties. Careful studies of the mechanism and extent of lanthionine formation have been made [4, 12, 14, 17]. While this compound is most often formed in highly alkaline solutions, it is known to occur in wool which has been boiled in solutions of pH as low as 7 [8]. Also, comparatively weak bases in mixed solvents have been found to convert cystine to lanthionine [21]. However, no systematic study of degradative effects of aqueous solutions of varying pH upon the stress-strain properties of wool fibers has been reported. Neither has the quantity of lanthionine formed under these conditions been correlated with the property changes.

In this investigation the effects of solutions of varying alkalinity on the wet physical properties of wool and the conditions under which lanthionine formation might occur have been evaluated. The results indicate the ease of producing alkaline degraded wool. Rather unexpected was the detection of considerable lanthionine in wool boiled in pH= 4.5 buffer solution and in wool heated in the atmosphere at 150° C.

[1] Part I: TEXTILE RESEARCH JOURNAL **26**, 781 (1956).

Experimental

Fiber stress-strain properties were measured with an Instron tester [5]. Selected fibers of New Zealand 44's fleece were mounted with Duco cement between cellulose acetate tabs. Samples exposed to 150° C. were mounted with an epoxy resin adhesive between Mylar tabs. Wet properties of the samples were determined by extension to 25% of the sample length in solutions buffered at pH = 6.7. The 1.0-in. samples were extended at a rate of 0.5 in./min.

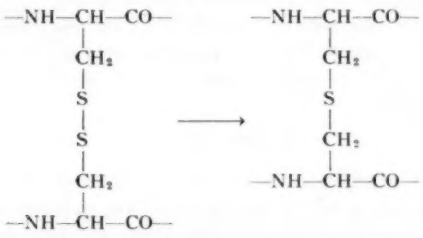
The pretested fibers and 0.5 g. of New Zealand 44's loose wool were immersed in buffered solutions contained in a constant temperature bath. After an immersion period of 24 hr. the samples were removed, washed, and placed in a pH = 6.7 buffer where the stress-strain curves were again measured. Ten fibers were used for each variation in exposure conditions. To permit ready comparison of results, all values were normalized.

The amino acid content of the loose wool sample was estimated by the previously described paper chromatographic procedure [7].

Discussion

Conversion of cystine to lanthionine by alkaline solutions in wool protein was well established through the isolation of lanthionine from alkali-treated wool [6]. Since this discovery, considerable effort has been devoted to elucidating the mechanism and quan-

titative aspects of the reaction. The exact mechanism of lanthionine formation is, however, still unknown. The intermediate formation of thiol groups [4], aldehydes [17], sulfenic acids, and 2-amino acrylic acid [1, 4, 12] has been proposed. Apparently, only 50% of wool cystine is reactive toward alkali [4] except under severe conditions.



Lanthionine is readily produced under certain other conditions. Boiling at pH 7 causes cystine loss [3, 13, 14, 20] and formation of a less than quantitative amount of lanthionine [4]. The production of lanthionine in wool by aqueous solutions of cyanides has been reported [4, 10, 16]. Zahn and Osterloh [21] recently reported that aqueous dioxane solutions of sodium bicarbonate cause lanthionine formation.

The action of solutions of varying alkalinity on the wet stress-strain properties and cystine-lanthionine ratios of wool has received little attention. A study by Cuthbertson and Phillips [4] was concerned with the effects of boiling buffer solutions on the sulfur balance of wool. Warner and Cannan [19] report that histidine, serine, and arginine are decomposed. According to Blackburn and Lee [2], boiling alkaline solutions cause destruction of cystine with quantitative formation of lanthionine but only limited degradation of serine and threonine.

In the present study pretested wool fibers were exposed to buffered solutions at controlled temperatures. At the end of a prescribed period the samples were removed, washed, and their wet stress-strain properties were determined. Simultaneously, a small sample of loose wool was exposed under the same conditions as the fibers. This was hydrolyzed and the quantities of lanthionine contained in each were estimated by paper chromatography [7].

Pretested fibers which had been exposed to solutions varying between pH = 7.0 and 12.25 for 24 hr. at 25° C. were extended wet 25% and the forces required were determined. In Figure 1 the force

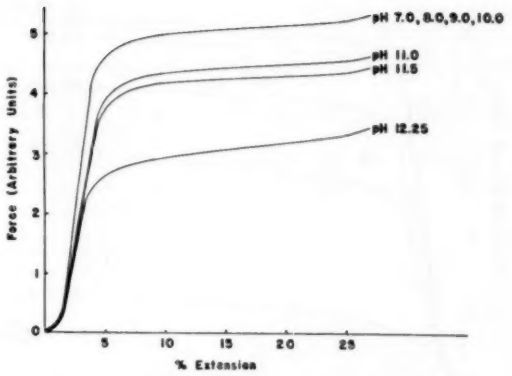


Fig. 1. Effects of solutions in 24 hr. at 25° C.

versus percentage extension curves of the wet fibers are plotted. Under these conditions the physical properties of the fibers were unaffected until the solution pH exceeded 10. Chromatographic examination of the wool hydrolysates showed that no lanthionine was produced until loss of physical properties occurred. In Table I the per cent decrease in force at 25% extension and estimated per cent cystine converted and lanthionine yielded are listed for samples exposed to each buffer solution.

An increase in solution temperature causes the expected large increase in the rate of alkali attack on wool. At 50° C. solutions having a pH as low as 9 affect the wet wool properties within 24 hr. At this temperature solutions of pH = 11.5 and pH = 12.5 degrade the fiber very quickly. In Figure 2 stress-strain curves of wet fibers after exposure to varying alkalinities at elevated temperature are shown.

The action of boiling aqueous solutions was studied. As expected, 24-hr. exposure at a pH = 6.7 causes a marked decrease in the wet fiber properties. Surprisingly, at a pH = 4.5, the amount of damage

TABLE I. Effects of Alkaline Solutions on Wool

24 hr. pH	% Decrease force at 25% extension	Estimated % cystine converted	25° C. Estimated % lanthionine yielded
7.0, 8.0, 9.0, 10.0	0	None	None
11.0	11	5–10	5–10
11.5	18	15–25	15–25
12.25	36	35–45	30–40

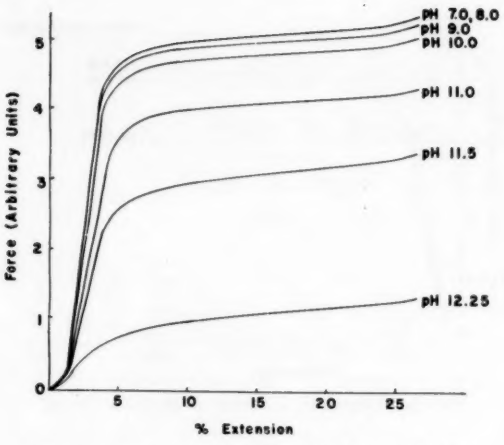


Fig. 2. Effects of solutions in 24 hr. at 50° C.

was almost as great as at pH = 6.7. The curves of these fibers compared with those of undamaged wool are shown in Figure 3. Paper chromatograms of the amino acids contained in these samples showed 25 to 40% of the cystine is lost and a considerable quantity (approximately 75% of the theoretical) of lanthionine is formed. Zahn [20] reported that a maximum of 20% cystine was lost in 24-hr. exposure to boiling water.

Atmospheric conditions at elevated temperature were also considered. After 24 hr. at 150° C., the yield point and force at 25% extension for the wet fiber were decreased 41 and 25%, respectively. Chromatograms of the amino acids showed an approximate loss of 30% in cystine and a comparable percentage of lanthionine produced. During these exposures no cysteic acid was produced although it might be expected to result through air oxidation. No changes were noted in the other amino acids contained in the hydrolysates. Zahn [20] found that serious damage was produced only when dry wool was heated at temperatures exceeding 150° C. The work of Mecham and Olcott [11] and of Lundgren and co-workers [9] indicates that new amide cross-links may be introduced in dry wool at high temperatures.

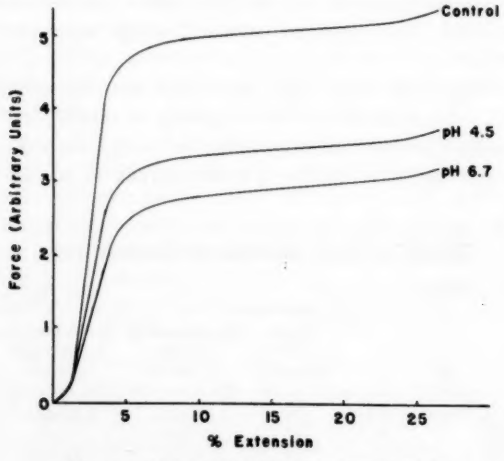


Fig. 3. Effects of boiling solutions in 24 hr.

Summary

The changes induced in wet fiber stress-strain properties and lanthionine formation in wool under a variety of conditions have been studied. It has been determined that

1. At room temperature, the properties of wet wool are not seriously affected until a pH of 10 is exceeded.
2. Any increase in temperature greatly accelerates degradation of wool caused by alkaline solutions.
3. Lanthionine formation in wool occurs at a pH as low as 4.5 in boiling water.
4. Cystine is partially converted to lanthionine when wool is heated to 150° C. in the atmosphere.

It has further been shown that wet stress-strain properties are modified approximately in proportion to lanthionine formation. Either is apparently a good measure of the degree of degradation caused by alkaline solutions.

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The Soiling Characteristics of Textile Fibers

Part II: The Influence of Fiber Geometry on Soil Retention[1]

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Abstract

The influence on soil retention of filament denier and cross-sectional contour of a series of man-made fibers has been studied. The fibers used included normal acetate (with the usual serrated cross section), circular cross-sectional acetate, nylon, Terylene,[2] and viscose rayon. Filament deniers varied from approximately 2 to 16. Soil content was determined by dissolving the soiled fiber in a suitable solvent and measuring the optical density of the resulting suspension.

In general, soil retention increases with decreasing filament denier, and for any one type of fiber, e.g., acetate, circular cross-sectional fibers retain less soil than those of similar denier but having a serrated cross section. Soil retention by any one type of fiber is a linear function of the gross surface area of the filaments. There are differences in soil retention by various chemical types of fiber that apparently cannot be related to differences in physical size and shape of the filaments. The influence of static electricity on soiling is not clear, soil retention showing no correlation with the magnitude of the electrostatic charge. The visual appearance of soiled fibers is not necessarily indicative of the quantity of soil retained.

Introduction

In Part I of this series [12], some of the factors that contribute to the soiling of textile materials were discussed, and a method was described for measuring the "effective soil content" of soiled fibers. In the present work the soiling of a series of man-made fibers has been studied, and an attempt has been made to show the relation between soil retention and various physical characteristics of the fibers.

Several workers have contributed to the present knowledge of this aspect of the soiling problem. Masland [6] concluded that soiling is primarily a function of the diameter and cross-sectional shape of the fiber. Low denier fibers were found to retain more soil than those of higher denier, and this was attributed to the greater surface area per unit weight of the smaller fibers. Normal viscose rayon, having the usual serrated cross-sectional contour, retained more soil than did viscose rayon fibers of the same denier which had a smooth, circular cross section. Under the microscope the soil was seen to have collected largely in the channels or serrations of the

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[2] Polyester fiber manufactured by Canadian Industries Ltd.

normal viscose, while in the circular fiber the soil was distributed in a random manner over the surface.

Compton and Hart [1, 4, 5] have concluded that soiling is largely due to occlusion of soil particles in pits and crevices in the fiber surface, and that soil particles must be of such size as to fit into these indentations. They found that carbon particles of about 50 mμ diameter and smaller produced a much greater degree of soiling on cotton and other fibers than did particles of larger size. This is probably partly due to the greater absorption of light by the smaller particles, since the surface area of a given weight of soil increases rapidly as the particle size decreases. Nevertheless the sharp break in the curves at about 50 mμ suggests that there must also be a decrease in the quantity of soil retained as the particle size increases beyond a certain critical value.

The importance of very small particles in the soiling mechanism was also stressed by Salsbury et al. [9]. A sample of natural dirt (floor sweepings) was found to contain 17% by weight of particles of less than 1 μ diameter, but this 17% contributed 77% of the total surface area, and hence of the potential soiling capacity of the soil.

The effect of electrostatic attraction on soiling was shown by Rees [7]. Cotton fabrics mounted in metal frames were suspended in the air and connected to a source of d.c. voltage. The charged fabrics soiled more rapidly than those which were maintained at zero potential. The rate of soiling increased with increasing potential, and positively charged fibers soiled more rapidly than negatively charged fibers. On the other hand, Schappel [10] found no correlation between soiling characteristics and electrostatic properties in carpets made from various fibers and fiber blends.

Experimental

Materials

The fibers studied were obtained in the form of bright, continuous filament yarns, and are listed in Table I.

All the yarns, with the exception of the Terylene, were extracted for 24 hr. in a soxhlet apparatus with benzene, then rinsed thoroughly with distilled water, and dried. The Terylene was extracted for 3 hr. with petroleum ether (60–80° C.), then for 3 hr. with methanol, rinsed with water, and dried. All the yarns were conditioned at 70 ± 2° F. and 65 ± 2% R.H. prior to use.

The soil used throughout this work consisted of

TABLE I. Description of Yarns Used

Designation	Fiber type	Yarn denier	No. of filaments	Filament denier		Twist, turns/in.	Specific surface, m.²/g.
				wt.*	micro.†		
A-1	Normal acetate‡	160	80	2.0	1.9	0.4	0.23
A-2	"	148	40	3.7	3.6	0.4	0.20
A-3	"	155	20	7.7	7.7	0.2	0.13
A-4	"	154	10	15.4	15.2	0.3	0.11
A-5	Circular acetate§	173	76	2.3	3.4	0.4	0.17
A-6	"	640	150	4.3	5.0	2.8	0.14
A-7	"	1210	130	9.3	11.8	0.7	0.09
A-8	"	2210	120	18.4	23.5	0.2	0.07
N-1	Nylon	71	34	2.1	2.3	0.5	0.20
N-2	"	144	40	3.6	3.8	0.9	0.16
N-3	"	212	34	6.3	6.4	0.9	0.12
N-4	"	260	17	15.3	15.5	0.9	0.08
V-1	Viscose rayon	100	40	2.5	2.5	2.2	0.22
V-2	"	150	36	4.2	4.2	2.0	0.18
V-3	"	292	44	6.6	6.4	2.0	0.16
V-4	"	913	54	16.9	14.1	3.7	0.12
V-5	"	907	27	33.6	33.9	3.5	0.07
T	Terylene	253	144	1.8	1.7	0.8	0.22

* Filament denier = (yarn denier)/(number of filaments).

† Filament denier calculated from measurement of cross-sectional area.

‡ Normal acetate denotes the usual type of acetate fiber having a number of smoothly rounded lobes with shallow longitudinal channels between them.

§ Circular acetate refers to a specially spun acetate filament the cross-sectional outline of which was free of the lobes and channels present in normal acetate, although it deviated considerably from perfect circularity.

TABLE II. Percentage Analysis of Soil

Ether soluble (fatty matter)		3.7
Loss at 105° C. (moisture)		2.8
Loss at 500° C. (organic matter)		40.5
Residue at 900° C. (ash)		54.5
Composition of ash	SiO_2	46.3
	Al_2O_3	6.8
	Fe_2O_3	6.5
	CaO	10.4
	MgO	2.4

screened vacuum cleaner sweepings, prepared as described in the previous paper [12]. An analysis of the material is given in Table II. The soil was also conditioned at 70 ± 2° F. and 65 ± 2% R.H. prior to use.

Methods and Data

(i) *Soil retention.* In the previous work on soiling in which carpet yarns were used [12], the yarn, after soiling, was blown in a stream of air to remove loosely held soil, and was then chopped into short lengths. The chopped fiber was formed into a flat pad and its reflectance was read with a Photovolt reflectometer. The yarns used in the present work were of much smaller diameter and were not readily cut by the chopping machine. Also the time required to arrange a large number of small yarns in front of the fan for removal of excess soil by blowing rendered this method impractical. Furthermore, reflectance data were shown to be influenced by the optical properties of the fibers, and consequently it was necessary to apply a correction to the reflectance data when comparing the soil contents of different types of fiber. These difficulties have been eliminated in the soiling and evaluation techniques used in the present work.

The conditioned yarn was cut into lengths of about 4 in., and a 3-g. sample was transferred to a 1-pt. glass Launder-Ometer jar, care being taken to separate the individual yarns as far as possible to avoid clumping. The required weight of soil was added along with fifty ¼-in. steel balls, and the jar was rotated at 42 r.p.m. in the Launder-Ometer at room temperature for 15 min. The contents of the jar were then transferred to a brass dusting cage, identical with that described by Schwarz [11], and rotated in the Launder-Ometer for a second 15-min. period.

After reconditioning overnight, a 2.5-g. portion of the soiled fiber was weighed into a 250-ml. volumetric flask, and about 200 ml. of a suitable fiber solvent was added. (A slight variation of this procedure was used for viscose rayon. See below.) The flask was shaken until the fiber was completely dissolved. The volume was then made up to the mark with fresh solvent, and the contents of the flask were thoroughly mixed. The optical density of the resulting suspension of soil particles was read on a Fisher Electrophotometer using a 525 mμ (green) filter, with pure solvent in the reference cell. A reading was also obtained on a similar solution of the unsoiled fiber and this was subtracted from the reading on the soiled fiber. The entire procedure was carried out in triplicate and the results were averaged. The reproducibility was such that the average coefficient of variation for the whole series of measurements was 2.4%.

A somewhat similar method has been described by Harris, et al. [3] in which cotton, soiled with a graphite soil, was dissolved in a mixture of nitric and sulphuric acids and the optical density of the resulting suspension was determined. In the present work the use of mineral acids was avoided because of their probable effect on the type of soil used.

The solvents used for the various fibers are listed in Table III. The acetone, m-cresol, and o-chlorophenol were freshly distilled before use, the latter two being distilled under reduced pressure. The benzyltrimethyl ammonium hydroxide was obtained as a 35% solution in methanol.[3] This material was diluted with an equal volume of distilled water and distilled in vacuo until the volume was reduced to somewhat less than that of the original alcoholic solution. The concentration of quaternary base was determined by titration of a 1-ml. aliquot with 0.1 *N* HCl, and the concentration was adjusted to 1.8 *M* by the addition of the calculated amount of water. The soiled viscose rayon was dissolved in 125 ml.

TABLE III. Fiber Solvents and Correction Factors

Fiber	Solvent	Correction factor
Acetate	Acetone	1.69
Nylon	m-cresol	1.94
Terylene	o-chlorophenol	1.94
Viscose rayon	1.8 *M* aqueous benzyltrimethyl ammonium hydroxide	1.00

[3] Obtained from Mid-West Laboratories, 1952 West Irving Park Rd., Chicago 13, Ill.

of this solution by shaking for about 1 hr. and then stored in a refrigerator overnight. (The solubility of the viscose increases with decreasing temperature.) The volume was then made up to the mark with distilled water, which was added in small increments with vigorous shaking to avoid reprecipitating the dissolved viscose. The optical density of the suspension was read in the usual way, using a 0.9 M solution of the base in the reference cell. The used solvent was recovered by diluting with about $\frac{1}{2}$ its volume of methanol and filtering off the precipitated viscose. The filtrate was then concentrated as before and adjusted to 1.8 M.

According to the well-known Lambert law, the intensity I of a beam of light, after passing through a thickness t of material whose absorption coefficient is K, is given by the expression $I = I_0 e^{-kt}$ or $\log (I_0/I) = Kt$, where I_0 is the intensity of the incident beam. The scale of the Fisher Electrophotometer is calibrated to read directly in units which correspond to 100 $\log (I_0/I)$, and hence the difference between the readings on the soiled and clean fibers is proportional to $K - K'$ where K and K' are the absorption coefficients of the solutions of the soiled and clean fibers, respectively. $K - K'$ represents the increase in absorption coefficient due to the soil contained in 2.5 g. of soiled fiber.

In the previous paper [12], it was shown that $K - K' = GX$, where G is the weight of soil retained by a given weight of fiber and X is the specific absorbance of the soil. Hence, provided that the specific absorbance remains constant throughout, the net meter reading, i.e., the difference between the readings on soiled and clean fibers, is a measure of the weight of soil retained by the fiber. In the present case, however, the specific absorbance is not constant, but varies with the type of dispersing medium employed, owing presumably to a difference in degree of aggregation of the soil particles in the various solutions. This was shown in the following way. Varying weights of soil were dispersed in 1% solutions of each type of fiber in the appropriate fiber solvent, and the optical density was determined in the usual way. The results are given in Figure 1. The lines correspond to the equation $K - K' = GX$, in which the specific absorbance X is given by the slope of the line. The values of X are relative since the net meter reading gives only relative values for $K - K'$. It is apparent that the specific absorbance and hence the degree of dispersion of the soil is greatest in the aqueous solution and least in the phenolic solutions, the value of X being 225 for the aqueous benzyltrimethyl ammonium hydroxide solution, 133 for the acetone solution, and 116 for both the m-cresol and the o-chlorophenol solutions. In comparing the soil contents of various fibers, it is therefore necessary to compensate for the effect of the dispersing medium by multiplying the net meter reading by a factor which is proportional to the reciprocal of these specific absorbances. The correction factors are listed in Table III and were used to adjust all of the data reported.

The corrected values still do not represent actual weight of soil retained by the fiber since the retained soil is not necessarily identical with the original soil. It is probable that small particles are retained more readily than larger particles, and hence the specific absorbance of the retained soil would be expected to be higher than that of the original soil. Confirmation of this was obtained in one case. With most of the fibers a small amount of fiber was lost during

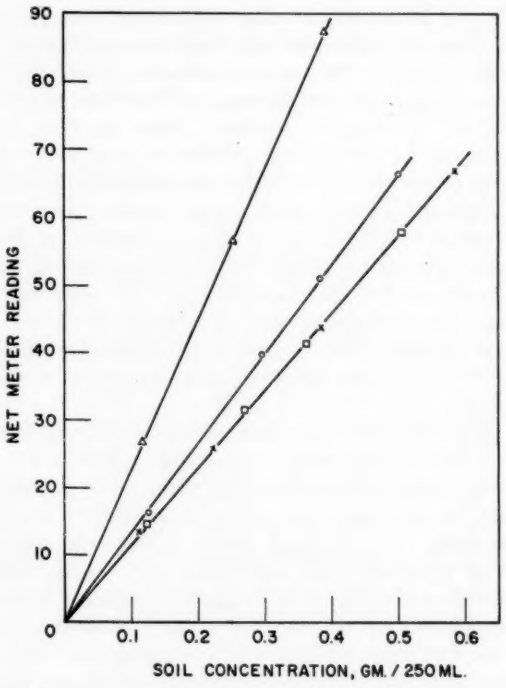

Fig. 1. Effect of dispersing medium on specific absorbance of soil. ⊙ 1% acetate in acetone, × 1% nylon in ⊡m-cresol, 1% Terylene in o-chlorophenol, △ 1% viscose rayon in 0.9 M aqueous benzyltrimethyl ammonium hydroxide.

the dusting operation so that determination of the soil content by reweighing the soiled fiber was not possible. With the Terylene fiber, however, there appeared to be no loss of fiber, and the weight of soil retained was estimated by reweighing the soiled fiber after dusting and reconditioning. From this weight and the corresponding optical density reading, the relative specific absorbance of the retained soil was calculated. The value obtained was approximately 150 as compared with 116 for the original soil in the same dispersing medium.

While the corrected values for soil content obviously do not represent the weight of soil retained, they do represent the weight of soil multiplied by the specific absorbance of the soil *as present on the fiber*. This term GX was previously defined [12] as the "effective soil content" of the soiled fiber. It would appear therefore that the quantity measured by the present technique is identical with that derived from reflectance readings in the previous work. The numerical values obtained are, of course, different in the two methods, since both methods give relative values only.

Following the terminology employed in the previous paper [12], the term "soiling level" is used to denote the weight of soil to which the clean fiber is subjected during the soiling test, i.e.,

$$\text{Soiling level} = \frac{\text{Weight of soil used}}{\text{Weight of fiber used}} \times 10$$

Soiling tests were carried out on each of the fibers listed in Table I at soiling levels of 0.5, 1.0, 1.5, and 2.0. The results are given in Figures 2 to 5 in which the relative effective soil content is plotted on logarithmic scales against the soiling level. In Figure 6, the effective soil content at a soiling level of 2.0 is plotted against the filament denier for each type of fiber.

(ii) *Specific surface.* The outlines of approximately 50 cross sections of each fiber were traced using a projection microscope at a magnification of $\times$ 1000. The area A and length of periphery p of each cross section were measured with a planimeter and map measurer, respectively. The filament deniers, calculated from the cross-sectional areas and the fiber densities are given in Table I. In most cases these values are in good agreement with those obtained by weight measurement. The values for the circular acetate fibers, however, are somewhat high and the reason for this is not known.

It was found that a plot of log p versus log A gave essentially straight lines over the range covered (Figure 7). The best line through the experimental points was calculated by the method of least squares, and the values of p corresponding to the measured values of A were read from the graph. The specific surface S was then calculated by means of the equation $S = p/A\rho$ where ρ is the fiber density, and S is measured in square meters/g., p in microns, and A in square microns.

The periphery measurements were possibly somewhat lacking in precision owing to the inability of the map measurer to follow exactly the intricate outlines of some of the fibers. Nevertheless, it is believed that the values for specific surface given in Table I represent approximately the gross external surface area of the various fibers.

The values found for nylon and Terylene agree very closely with values calculated for a circular filament of corresponding denier and density, while the values for normal acetate and viscose rayon are considerably higher than those of the corresponding circular filament, reflecting the deviation from circularity of these fibers. The values for circular acetate are slightly higher than the calculated values. It is interesting to note, however, that the specific surfaces of 3–4 den. filaments, as determined by low temperature nitrogen adsorption (viz., acetate 0.38, nylon 0.31, viscose rayon 0.98 m²./g. [8]), are somewhat higher than the above values for nylon and acetate, and considerably higher for viscose rayon. This seems to indicate that in all of the fibers, but particularly in the viscose rayon, there are areas, possibly submicroscopic crevices and pits, that are available to nitrogen molecules, but which are not measurable by the techniques used in the present work.

Discussion

Filament Denier

The data represented in Figures 2 to 5 show that, as might be expected, the soil content of the soiled yarn increases with increasing soiling level. It is also apparent that, in accord with the findings of Masland [6], the degree of soil retention in general decreases with increasing filament denier, particularly at the higher soiling levels. At the lower soiling levels there are some deviations from this general trend, notably in the fibers A-6, V-4, and V-5, the soil contents of which are higher, and N-1, the

soil content of which is lower than would be expected from the general trend. Reference to Table I indicates that the fibers A-6, V-4, and V-5 are slightly more twisted than the other fibers. It will be shown in Part III of this series that a moderate amount of twist leads to an increase in soil retention owing to the entrapment of soil in the interfiber spaces. While it is probable that the small amount of twist in the above-mentioned yarns results in some increase in soil retention, it seems unlikely that the relatively high soil retention of the V-4 fiber can be explained on this basis, and as yet no satisfactory explanation for this, or for the apparently low soil retention of the N-1 fiber, has been found.

The effect of filament denier on soil retention at a soiling level of 2.0 is shown more clearly in Figure 6. The general trend toward decreased soil retention with increasing denier is clearly indicated. Curves of similar form, but with a somewhat greater scattering of the experimental points, are obtained

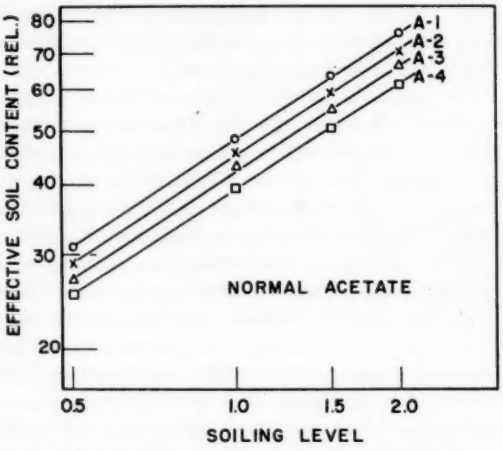

Fig. 2. Soil retention of normal acetate yarn.

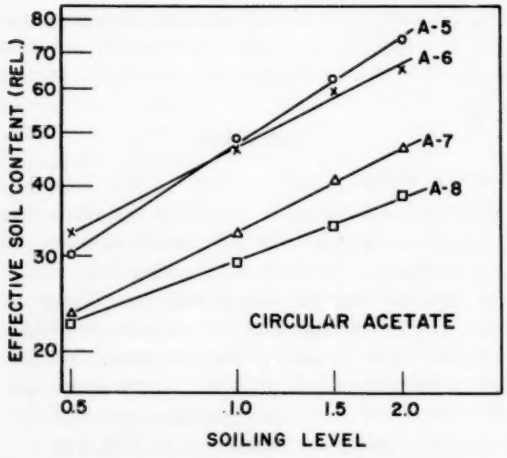

Fig. 3. Soil retention of circular acetate yarn.

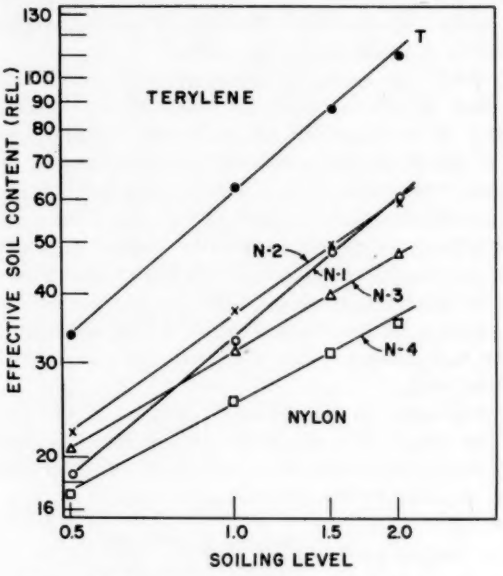

Fig. 4. Soil retention of nylon and Terylene yarns.

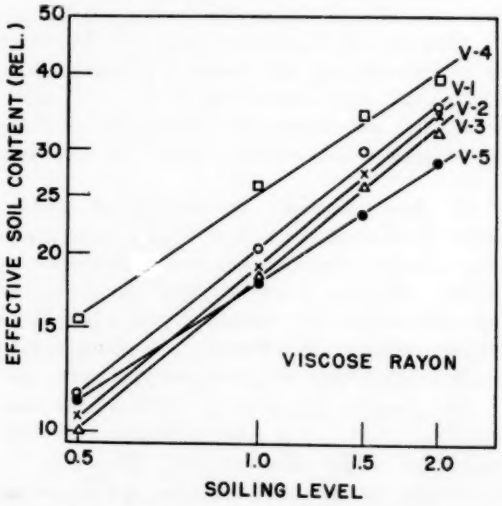

Fig. 5. Soil retention of viscose rayon yarn.

when the soil content at the lower soiling levels is plotted against filament denier.

Chemical Type versus Physical Shape

Figure 6 also gives some indication of the relative soilability of the various fiber types. Over the range of deniers studied the order of increasing soilability is viscose rayon (except for the V-4 yarn), nylon, circular acetate, normal acetate, and Terylene. Terylene yarn of only one D/F (i.e. 1.8) was available, but it is probable that yarns of higher D/F would also soil more readily than normal acetate of corresponding D/F.

These results in some instances confirm Masland's findings [6] that smooth circular fibers retain less soil than those having an irregular or serrated cross section. Thus the nylon, which is a smooth, circular fiber, and the circular acetate retained less soil than the normal acetate. On the other hand, the Terylene, which is also a smooth, circular fiber retained more soil than any of the other fibers, and the highly serrated viscose rayon fiber retained the least. The obvious conclusion to be drawn is that for any one type of fiber, less soil is retained by a smooth, circular filament than by a filament with an irregular or serrated cross-sectional contour, but that the chemical type of the fiber may have a greater influence on soil retention than has the physical shape of the filament. (It is to be noted that Masland's work was based very largely on a comparison of normal viscose with circular viscose rayon, although he did include a few wool fibers.)

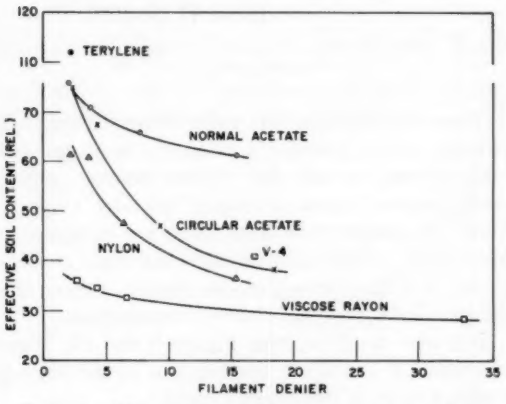

Fig. 6. Effect of filament denier on soil retention.

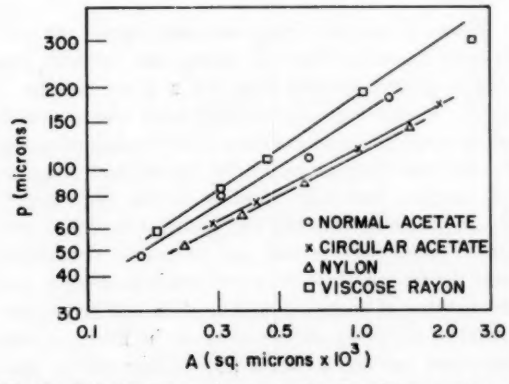

Fig. 7. Relation between cross-sectional periphery and area.

Channels or Striations in the Fiber

A fiber of irregular cross-sectional contour, as compared with a circular fiber of corresponding denier, provides additional soil-holding sites owing to soil entrapment in the channels or striations [6, 9].

The curves shown in Figure 7 may be defined by an equation of the type $p = kA^n$, where k and n are constants. The values of k and n for each fiber type and the calculated values for a circle are given in Table IV.[4]

The constant k represents the periphery at unit area (or in this case, at an area of $1 \times 10^3 \mu^2$) and hence is an indication of the deviation from circularity of the cross sections of the various fibers. It may be seen that the value of k for nylon filament is very close to that of a perfect circle, while the values for normal acetate and viscose rayon are considerably higher. The value of k is influenced by the number of indentations in the cross-sectional contour, i.e., by the number of striations or channels in the filament. A high value of k is not necessarily

TABLE IV. Values of the Constants k and n

Fiber	k	n
Normal acetate	154	0.61
Circular acetate	121	0.52
Nylon	113	0.51
Viscose	189	0.67
(Circle)	112	0.50

[4] In Figure 7, the unit of measurement of A (thousands of square microns) was chosen so that the values of k could be read from the graph without extrapolation, i.e., $k = p$ where $A = 1$.

indicative of a large number of indentations, however, since any deviation from circularity results in an increase in the value of k, e.g., for a square, $k = 126$.

For any given geometrical shape, $p/\sqrt{A} = \text{const.}$ or $p = kA^{0.5}$, regardless of the size of the figure. The fact that the value of n for all of the fibers is greater than 0.5 indicates that, as the fibers increase in size, the cross-sectional contour is not merely a magnified image of that of the smaller sizes, but also increases in complexity, i.e., in deviation from circularity.

However, it is not the number of indentations in the cross-sectional contour that determines the soil-holding capacity of the fiber, but rather the total *length of channel* in a given weight of fiber. If N is the number of indentations in the cross-sectional contour of a filament of length l, then the total length of channel will be Nl and the weight of the filament will be $Al\rho$ (ρ = fiber density). The length of channel in unit weight of fiber (C) will thus be $N/A\rho$. An approximate value for N can be calculated in terms of measurable quantities if it is assumed that the increase in cross-sectional periphery over that of a circle of the same area is proportional to the number of indentations in the cross-sectional contour, i.e., $N = q(p - p_c)$, where p is the periphery as measured, p_c is the periphery of a circle having the same area, and q is a constant. This assumption is open to some question since, as pointed out previously, the increased periphery may be the result of any deviation from circularity. However, provided the results are interpreted with caution, it is believed that the assumption is justified as a means of obtaining a first approximation of N. Hence

$$C = \frac{N}{A\rho} = \frac{q(p - p_c)}{A\rho} = q(S - S_c)$$

where S is the specific surface of the fiber as measured and S_c is the specific surface of a circular fiber having the same cross-sectional area and the same density as the experimental fiber. It can be shown that $S_c = 3.54/\rho\sqrt{A}$ and hence

$$C = q\left(S - \frac{3.54}{\rho\sqrt{A}}\right).$$

Calculated values of c/q (i.e. relative values of C) are shown in Figure 8.

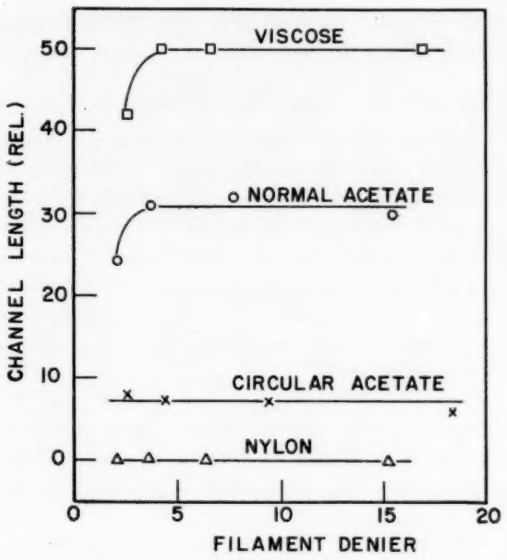

Fig. 8. Effect of filament denier on channel length per unit weight of fiber.

These data indicate that nylon is free of channels, circular acetate contains a relatively small number, while normal acetate and viscose contain progressively greater lengths of channel per unit weight of fiber. In general these conclusions are confirmed by microscopic examination of the fiber cross sections, except that the contour of the circular acetate fiber did not have any well-defined indentations.

It is also apparent from Figure 8 that the length of channel is essentially independent of the filament denier, except at the lowest deniers.

Surface Area

Fibers of irregular cross-sectional contour not only provide channels which can entrap soil, but also provide a greater surface area for a given weight of fiber. It has been shown that most fibers exhibit many small pits and crevices when examined under the electron microscope [2, 9]. Hart and Compton [4] suggest that soil retention is due very largely to the occlusion of small soil particles in these crevices. Since the crevices are randomly distributed over the fiber surface, it is reasonable to assume that the number of such soil-holding sites will be proportional to the gross surface area of the fiber. Hence there are two independent fiber characteristics that appear to influence soil retention, viz. (*a*) the pres-

ence of channels or striations, which can accept particles of varying size, and the influence of which is essentially independent of the filament denier, and (*b*) the presence of pits and crevices, which accept only the smaller particles, and the number of which, in a given weight of fiber, increases with increasing surface area or with decreasing filament denier.

In Figure 9, the effective soil content at a soiling level of 2.0 is plotted against the specific surface for each fiber. In spite of some scattering of the experimental points, it appears that there is an approximately linear relationship between these quantities over the range of surface areas covered, and that differences in soil retention by various fiber types still exist when fibers of similar surface area are compared.

The curves shown in Figure 9 may be represented by an equation of the form $Y = mS + b$, where Y is the soil content, S is the specific surface, m is the slope of the curve, and b is the point at which the curve, when produced (dotted lines in Figure 9), cuts the axis of Y. This is the type curve that would be expected from the foregoing discussion of retention mechanisms. The total soil content is made up of a fixed quantity of soil, held in channels or striations, which is independent of the surface area or filament denier (represented by b), and a variable quantity of soil, held in pits and crevices, which is proportional to the surface area (represented by mS).

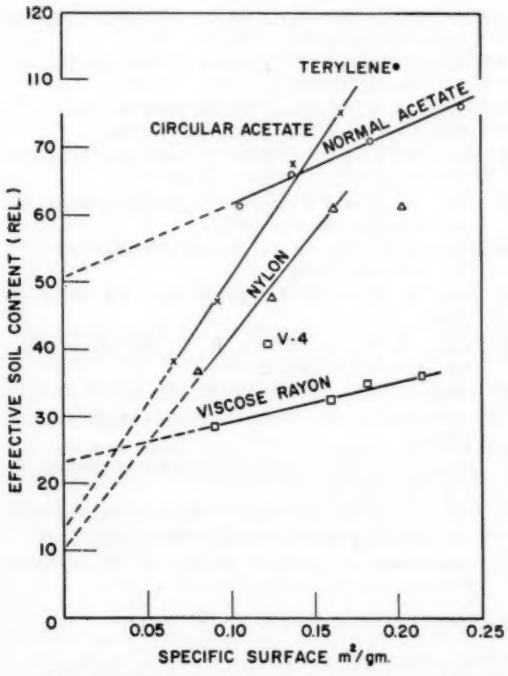

Fig. 9. Effect of surface area on soil retention.

While it is thus possible to predict the type of curve in a qualitative manner, quantitative agreement with expected results is lacking in some cases. For example, the curves for nylon and circular acetate would be expected to pass through the origin ($b = 0$) since these fibers do not contain channels. The small values of b obtained for these fibers (10 and 12, respectively) may be the result of a slight experimental error in the specific surface measurements, or of the retention of a small fixed quantity of soil by some mechanism other than entrapment in channels.

Viscose rayon fibers contain a greater length of channel per gram than do normal acetate fibers, and hence it is reasonable to expect that, in the absence of other influences, viscose rayon would become more heavily soiled than the normal acetate. Yet the data presented in Figures 6 and 9 indicate that this is not the case. Comparison of the values for specific surface obtained by nitrogen adsorption with those obtained microscopically suggests that the viscose rayon contains a greater number of small crevices than does the normal acetate fiber, and hence again the viscose would be expected to soil more heavily than the acetate. (This conclusion is perhaps open to some question, since the nitrogen adsorption and microscopic measurements were obviously not carried out on the same fibers. It is assumed that viscose rayon from different sources would have similar characteristics.) Hence it would appear that there is some property, related to the chemical type of the fiber, and apart from its physical size and shape, that influences the retention of soil.

Static Effects

Little mention has so far been made of the high soil retention of the Terylene fiber. The effect of static electricity was very evident during the soiling of this fiber. During rotation in the Launder-Ometer jar, the fibers became highly electrified, as indicated by the manner in which they clung to the glass jar and to the tweezers used to handle them. There was no evidence of loose soil in the bottom of the jar, as there had been with all of the other fibers,

and on reweighing the soiled fiber after dusting, it was found that about 95% of the original soil was retained even at the highest soiling level. Since practical experience has shown that static effects may lead to troublesome soiling of textile materials, particularly some of the newer synthetic fibers, it is tempting to conclude that the high soil retention of the Terylene fiber shown in Figures 4 and 6 is the result of static electrification. Yet nylon, which is also subject to static effects, exhibits a low degree of soil retention. (Salsbury et al. [9] give the following data for the magnitude of the electrostatic charge on various fibers: viscose 0–2; acetate 6–7; nylon 100; Dacron [5] (which is similar to Terylene) 500). In accord with the findings of Schappel [10], it appears that there is no correlation between soil retention and the magnitude of the static charge.

It is apparent, however, that some property other than the size and shape of the filaments contributes to soil retention. Both the nylon and the Terylene, being smooth, circular fibers would be expected, in the absence of other influences, to be relatively soil resistant.

Visual Appearance of the Soiled Fibers

Portions of approximately 2 *D/F* and 15 *D/F* soiled fiber of each type were graded according to apparent degree of soiling by eight independent observers. The agreement between observers was remarkably good, the fibers being placed in the following order of decreasing "dirtiness"; Terylene, nylon (viscose and normal acetate, about equal), circular acetate. Comparison of these results with the data of Figure 6 indicates that the order of decreasing soilability is quite different in the two cases. The viscose rayon and the normal acetate fibers, which appear visually to be soiled to about the same extent, contain very different amounts of soil on the basis of effective soil content. Likewise the nylon fiber appears visually to be much more heavily soiled than is indicated by the effective soil content. This characteristic of nylon was noted in the previous paper [12]. Based on reflectance readings (which have been found to correlate well with visual observation), the nylon was soiled more heavily than any of the other fibers studied; yet on the basis of effective soil content, the nylon was shown to have retained less soil than did several of the other fibers. This was attributed to the effect of delustrant, since the nylon was composed of bright filaments, whereas the other synthetic fibers were delustered. However, in the present case, none of the fibers contain delustering pigment and hence some other explanation must be sought.

It has been suggested that soil particles may become concealed from view in deep serrations or in the case of wool fibers, under the scales. While this may be true to some extent, and for some fibers, it does not explain the fact that nylon, which has neither scales nor deep serrations, showed considerable deviation between visual appearance and actual soil content.

[5] Du Pont polyester fiber.

Acknowledgment

The authors are indebted to Canadian Celanese Ltd., Drummondville, Quebec, Canadian Industries Ltd., Montreal, Quebec, Courtaulds (Canada) Ltd., Montrol, Quebec, and DuPont of Canada Ltd., Kingston, Ontario, for supplying the yarns used in this work.

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National Cotton Council of America

Fifth Chemical Finishing Conference

The following nine papers were presented October 3 and 4, 1956, in Washington, D.C. Other papers presented appeared in the February issue of TEXTILE RESEARCH JOURNAL.

Protective Treatments for Cotton Awnings

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Abstract

The cooperative research program of the USDA's Southern Utilization Research Branch and the National Canvas Goods Manufacturers' Association for improvement in the durability of cotton awnings and other outdoor fabrics is described, and the preliminary weathering exposure studies performed under the joint program are presented. Data were obtained on a number of laboratory experimental and proprietary weather-resistant treatments for awning fabrics that had been exposed to outdoor weathering. Laboratory-prepared coatings and standard commercial coatings are compared after twelve months' weather exposure. Data are presented to demonstrate the increase in weather durability of heavy duty cotton sewing threads treated by the vat dyeing and acetylation process.

Introduction

In recent years the competitive position of canvas awnings in the total awning field has been undergoing a subtle though noticeable change primarily due to increased competition from wood, metal, and synthetic materials. The position of cotton in this field would be strengthened if its resistance to solar radiation and microbiological degradation could be increased, and the protective and decorative performance of the awning coating compositions improved. With this objective, an industry fellowship for research on cotton textiles has been established by the National Canvas Goods Manufacturers' Association (NCGMA) at USDA's Southern Utilization Research Branch in New Orleans, La. The purpose of the fellowship is to conduct investigations aimed at improving the performance of canvas goods and sewing threads in awnings, tents, and tarpaulins. The experimental work has been integrated into the Southern Laboratory's broad program of research to maintain and extend the utilization of cotton. This paper describes the initial work conducted under the cooperative research program.

The Fellowship and Research Committee of the Association outline the following reasons for failure of cotton awnings:

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[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

1. Loss of strength of the awning fabric
2. Loss of decorative value
3. Deterioration of sewing threads

All three problems could be produced by

1. Solar radiation
2. Microbiological action
3. Airborne acids
4. Miscellaneous factors, such as gutter overflow and rust staining

Sunlight is an important problem in weathering and is encountered universally. Microbiological action and airborne acids are restricted to areas of relatively moist warm temperatures and industrial activity, respectively. However, it was the unanimous opinion of the NCGMA Research Committee that these two are responsible for almost all unusually rapid failures of cotton awnings. On recommendation of the Committee, research on the airborne acid problem was deferred until preliminary studies on the sunlight and microbiological problems had been completed.

The present paper describes the study of finishing materials for coated cotton awnings, and cotton sewing thread, to obtain optimum weather resistance. There are three separate factors that constitute the conversion of cotton duck into coated or striped awnings. These factors are (1) the protective treatment of the base fabric, (2) the coating applied to the treated base fabric, and (3) the sewing threads used to fabricate the coated fabric into a finished awning. Improvements in one or all of these should undoubtedly lead to an increase in the performance or useful durability of the final product.

Test Materials and Methods

The cotton materials used were a scoured 8-oz. army duck, and scoured 12/4 and 16/4 sewing threads. The duck was alkali-scoured on a dye jig, and the threads in a package dyeing machine, to remove the impurities and noncellulose constituents. Prior work by Dean [2] has shown that the average strength losses of gray cloth were higher, and individual losses more erratic, than those of the scoured fabric when exposed to the same weather conditions. These results were attributed to the presence of noncellulosic materials of relatively greater biological susceptibility, which allow nonuniform, seasonally influenced attack by microorganisms. All fabric investigations were made on the scoured 8-oz. army duck unless otherwise stated.

Weather exposure tests were conducted in New Orleans, Louisiana, in an unshaded location particularly free from airborne industrial contaminants. The samples were exposed on open-backed wooden racks facing south at an angle of 45° from the vertical, and at a minimum distance of 30 in. above the ground. Samples were removed for observation and breaking strength tests at intervals of 2 months. Breaking strength tests were made by the conventional methods for raveled strips and by single thread breaks for yarn. For convenience, all are reported as percentages of the materials as first exposed, whether untreated or treated.

Treatments and Coatings

Duck Treatments

In almost all cases the fungicides were applied from solution in mineral spirits to samples of duck 48 × 8 in., with the long dimension in the direction of the warp. The fungicides were all commercial products and were applied in the following concentrations: copper 8-quinolinolate, 0.18% copper as metal (copper-8); zinc 8-quinolinolate, 0.4% zinc as metal (zinc-8); cupri-magnesium dihydro abietyl amine 8-hydroxy-quinolinium 2-ethylhexoate, 0.6% copper as metal (copper amine complex); zinc-magnesium dihydro abietyl amine 8-hydroxy-quinolinium 2-ethylhexoate, 0.6% zinc as metal (zinc amine complex); bis(5-chloro-2-hydroxyphenyl)methane, 1.0% (dichlorophene). Names in parentheses represent abbreviations used throughout this paper. The urea formaldehyde resin was a water-soluble monomer applied from an aqueous solution and heat cured for 3 min. at 300° F., to give a 6% take-up of the resin on the dry weight of the fabric. The urea formaldehyde–copper 8-quinolinolate treatment was applied and cured, as above; the fungicide being present in a water emulsifiable form dispersed in the resin solution. The commercially treated fabric was a sample of 8-oz. duck treated with a mineral dye and fungicide combination.

Duck Coatings

All coatings were applied to the previously treated cotton duck by means of a laboratory modified coating machine, utilizing the doctor blade principle. The coatings, with two exceptions, were formulated on an approximate pigment volume concentration of 35%. The vehicles included were: a long oil soya modified alkyd, an air dry silicone alkyd, a tung oil

phenolic spar varnish, an oil modified styrenated alkyd, an air dry oil modified epichlorohydrin bisphenol (epoxy) resin, and an essentially pure epichlorohydrin bisphenol (epoxy) resin. The pigment portion consisted of 80 parts high-grade red iron oxide and 20 parts calcium carbonate. Dibutyl phthalate to the amount of 10% based on vehicle solids weight was utilized as a plasticizer. A fungicide (dichlorophene) in the equivalent of 2.5 weight per cent of solid vehicle was included. Aluminum stearate in small quantities and in combination with mineral spirits or xylol aided the viscosity and resultant fabric penetration control. Lead, cobalt, calcium, and manganese naphthenate dryers were included in recommended percentages where needed.

The polyvinyl chloride latex formulation was one specifically recommended by the resin producer as suitable for awning coating and contained a resin-pigment ratio of 60 to 50 parts by weight. This coating was cured for 10–12 min. at 375° to 400° F. The commercial coating formulation was supplied, ready to apply, by an awning striper and was reputedly a high-grade awning coating based primarily on natural vegetable drying oils with a red iron oxide pigmentation. The color of all of the striped samples was, before exposure, almost identical.

Sewing Threads

A survey of canvas awning fabricators [4] has indicated that dissatisfaction with the performance of cotton sewing threads was one of the most frequently mentioned complaints. Fifty-five per cent of the firms and individuals surveyed listed the durability of cotton threads as a major point for improvement. This failure of cotton threads is principally the result of degradation caused by either mildew or sunlight, or both, depending on the conditions of exposure. Previous work on cotton yarns described by Berard [1] has demonstrated that one of the most promising treatments to resist the combined effects of weather is achieved by first dyeing cotton with certain light-stable vat dyes and following this with partial acetylation. A set of 12/4 and 16/4 cotton sewing threads were scoured, dyed an 8% shade with Anthraquinone Vat Khaki 2G, and then acetylated to approximately 22% acetyl. Half of these threads were then glazed by a commercial thread manufacturer.

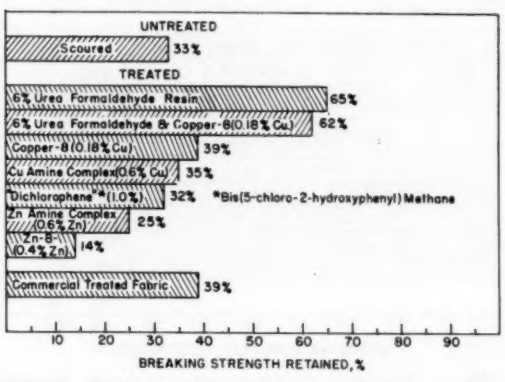

Fig. 1. Retention of strength after 12 months weathering for various protective treatments on uncoated awning canvas.

Results Obtained

The strength retentions of the fungicidally treated and untreated 8-oz. army duck for 12 months of exposure to weather are shown in Figure 1. The urea formaldehyde alone, and urea formaldehyde plus copper-8, had strength retentions of 65 and 62%, respectively. The copper-8 and commercially treated samples had 39% strength retentions, while the copper amine complex and "dichlorophene" samples showed strength retentions of 35 and 32%, respectively. The zinc amine complex and zinc-8 compounds offered no protection against actinic breakdown with 25 and 14% strength retentions, which were lower than the untreated control that had retained 33%.

Visual examination of these samples after exposure revealed that the urea formaldehyde resin alone did not suppress the growth of staining noncellulose-destroying microorganisms, while the samples containing fungicides were essentially free of microbiological attack.

The results of a full year weather exposure of commercial awning fabrics and those of a laboratory prepared coating, and a commercial coating, both applied to urea formaldehyde–copper-8 and copper amine complex treated fabrics, are shown in Figure 2. The laboratory prepared coating, using the long oil soya alkyd resin as the vehicle, and the commercial coating, based primarily on natural drying oils, applied to the urea formaldehyde–copper-8 treated duck had strength retentions of 92 and 80%, respectively. These same coatings applied to the copper amine complex treated duck showed 80 and 68% strength retentions. The commercial awning fabrics retained about 67% after a full year of exposure.

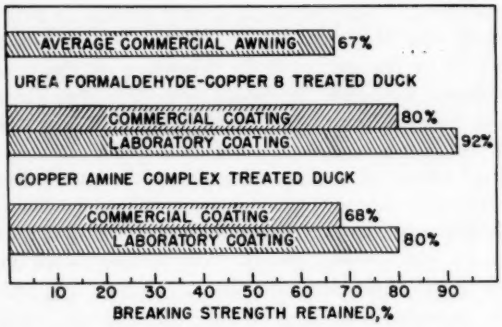

Fig. 2. Retention of strength after 12 months weathering for a laboratory-prepared coating and commercial coating.

These results indicate that protective treatments which are applied to duck fabrics, before coating, have an important influence on the durability of the awning.

The comparative performance of laboratory coatings that were prepared with different vehicles, after 12 months weather exposure, are shown in Figure 3. These coatings were formulated as previously described, and were applied to urea formaldehyde–copper-8 treated duck. The long oil soya alkyd resin had 92% strength retention, while the silicone alkyd, tung phenolic varnish, styrenated alkyd, and the commercial awning coating, showed strength retentions of 84–80%. The heat-cured polyvinyl chloride resin, the oil-modified epoxy resin, and the pure epoxy resin, had 77–74% strength retentions, which were just slightly better than commercial awning fabrics that averaged about 67%.

No matter how successful various treatments and procedures applied and performed in the laboratory may appear when tested on a small scale, there is always the possibility that conversion to full-scale commercial equipment and practice will disclose problems that may render difficult the transition from laboratory to plant. However, in the present instance this does not appear to be a problem. With the cooperation of a commercial awning striper, several hundred yards of canvas were striped using coatings based on the alkyd resin formulation, previously described, and full-size unmodified commercial striping equipment. The awning fabrics thus striped dried for handling in about 12 hr. in comparison with the older type coating which required 72 to 96 hr. for complete drying.

In these initial studies, only limited attention was paid to the influence of the pigment portion of the coating formulation on the durability of the finished awning fabric. However, a number of samples of canvas coated with compositions containing various pigments were exposed. Though the results of these tests were not conclusive, there was a firm indication that the type and color of pigments is an important factor in the weathering performance of the coated duck. Certain inorganic yellows and greens, predominantly those containing varying amounts of lead chromate, appear to offer considerably greater protection than the organic greens, yellows, and reds. The only inorganic red exposed, red iron oxide, appeared to offer appreciably more protection than the organic pigment, but less than the chromate-containing inorganics. A series covering at least one of each of the classes and types of coating pigments and extenders, as published by the Scientific Section of the National Paint Varnish and Lacquer Association [3], are now undergoing testing, and will be reported in a future paper.

Figure 4 illustrates that after 10 months of outdoor exposure the acetylated vat-dyed 12/4 glazed threads showed the high strength retention of 79%, and the soft yarn had retained 51% of its original strength. The acetylated vat-dyed 16/4 glazed thread showed 73% strength retained and the same size in soft finish 51%. Both the 12/4 and the 16/4 natural glazed sewing threads had 33% strength retention.

One of the problems that a treatment of thread will always produce is that of change of performance

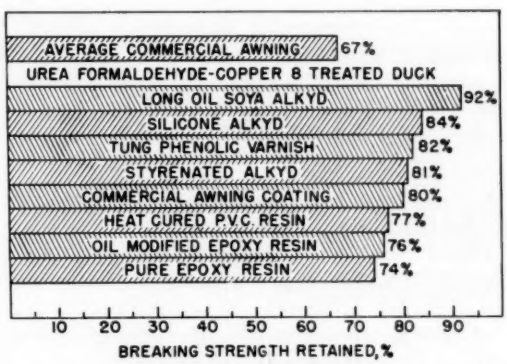

Fig. 3. Retention of strength after 12 months weathering for laboratory-prepared coatings containing different vehicles.

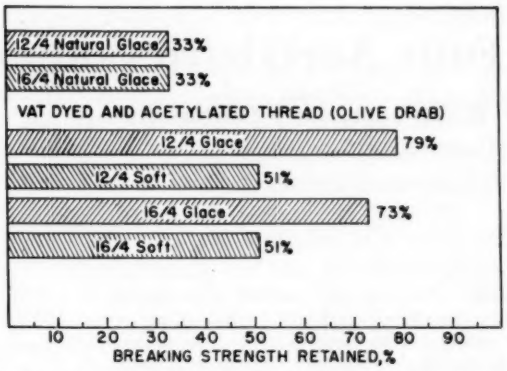
12/4 Natural Glace 33%
16/4 Natural Glace 33%
VAT DYED AND ACETYLATED THREAD (OLIVE DRAB)
12/4 Glace 79%
12/4 Soft 51%
16/4 Glace 73%
16/4 Soft 51%
10 20 30 40 50 60 70 80 90
BREAKING STRENGTH RETAINED,%

Fig. 4. Retention of strength after 10 months weathering for vat-dyed and acetylated sewing threads.

in actual sewing. It is difficult to conceive of any treatment that would not alter to some degree the sewing characteristics of the original thread. However, the 16/4 and 12/4 treated sewing threads, described above, have been tested without adverse comment on their sewing performance by two cooperating awning fabricators. The threads performed satisfactorily in both sample strip seam sewing tests and in factory fabrication of nine full-size residential awnings, using standard commercial sewing machines. The fabrics used in these tests were the experimental coated fabrics prepared in the previously described pilot plant run. These experimental awnings are now undergoing service testing in actual residential conditions and usage.

Conclusions

It has been shown that the over-all performance of coated cotton awnings can be improved by utilizing new materials and treatments now available.

When exposed under the subtropical climatic conditions of New Orleans, La., a canvas treatment consisting of 6% urea formaldehyde resin plus copper-8-quinolinolate (0.18% Cu as metal) has been shown to have greater weathering durability than standard commercial awning fabric treatments. Fabrics coated with formulations based on alkyd-type synthetic resins have withstood weather exposure to a greater degree than the conventional fabrics coated with natural drying oil-base formulations. A considerable reduction in time required for the coated fabric to dry has been obtained by the use of these alkyd resins.

Treated sewing threads have been prepared using the acetylated vat-dyed and glazed treatments that have shown an outdoor service durability of more than twice that of the conventional threads tested.

Results of weather exposure have indicated that the pigmentation of the coating formulation, as well as the vehicle, exerts a considerable influence on the durability of the coated fabric, and that further research is necessary to determine the optimum materials and concentrations for greatest canvas awning durability.

Acknowledgment

The authors wish to express their appreciation to the Analytical Physical-Chemical and Physics Section for many tests.

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A Preliminary Report on Fully Acetylated Cotton

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Abstract

Fully acetylated cotton (FA cotton), a chemically modified cellulosic fiber made from cotton and retaining its fibrous form, is described. A small-scale method of preparing a completely or nearly completely substituted product from cotton raw stock, yarn, or fabric by the application of acetic anhydride and perchloric acid catalyst in a diluent which minimizes the tendency of the product to dissolve, is reported. Its general properties and behavior in laboratory tests show it to have many superior properties to previously known cellulosic fibers, including partial acetates and triacetates. FA cotton has good tenacity, both wet and dry, and flex-abrasion endurance; it has some thermoplasticity, yet shows no sticking at ironing temperatures below 250° C.; it has low moisture regain and is dyeable with ordinary acetate colors. Work in progress indicates that treatment of yarn and fabric may be carried out satisfactorily in commercial-type stainless steel equipment.

Introduction

New and often specialized qualities are needed in cotton to improve its competitive position in household, apparel, and industrial uses. One approach to obtaining these qualities is chemical treatment which changes the composition of cellulose yet retains the fibrous form of the cotton. Most chemical modifications of cotton which have been studied to any great extent in this country are partial modifications, such as partial acetylation, in which only the hydroxyl groups in the amorphous portions of the fiber, and in those accessible groups presumably on the crystallite surfaces, are reacted. Typical products, which are commercially available, contain about one acetyl per anhydroglucose unit, though frequently much less. A product of similar average composition, but differing in method of preparation and in certain properties has also been available in Europe for many years. The continuing commercial production of these chemically modified cottons indicates that products of this type can be successfully introduced if they have improved properties which justify the cost of treatment. This has encouraged the preparation and evaluation of other chemically modified cottons [6]. They also provide a standard of comparison for any new chemically modified cotton. The member of this fascinating family which is the subject of this paper is fully acetylated cotton, or simply FA cotton. While apparently related to partially acetylated (PA) cotton, fully acetylated cotton has some properties which are more interesting and attractive from many points of view. This paper describes the initial work of preparation and some exploratory evaluations conducted at the Southern Regional Research Laboratory.

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[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

Preparation

Chemical treatments for the complete acetylation of cotton cellulose which retain the fibrous form of the original material, as distinguished from those which lead to dissolution of the cellulose acetate as complete substitution is approached, have appeared in the chemical literature. In the classical method of Hess [10], cotton is boiled in a mixture of acetic anhydride and pyridine. Products of the desired chemical composition may be obtained, but these are generally browned and degraded, and they do not retain the basic textile properties of flexibility and strength. Variations such as the addition of alkaline catalysts (e.g., postassium acetate), and more recent modifications of the reaction conditions such as the addition of N,N-dialkyl amides (e.g., dimethyl formamide) and gamma-valerolactone, as used by Blume and Swezey [2], could not be made to yield

products of promising textile properties when applied to cotton raw stock.

Somewhat better results were obtained in trials when the reaction conditions described in the patent literature [4] for producing the triacetate from cotton cellulose, using zinc chloride as a catalyst, were applied. Though the textile properties of the product seemed better than those obtained with the higher temperature methods, the long period of treatment required, 15 hr. or so, was not attractive. The use of stronger catalysts such as perchloric acid, which are also mentioned in the British patent, was investigated.

Experience with the development of the perchloric acid catalyst method used in partial acetylation processes [3, 5, 8] suggested that more desirable reaction conditions would be obtained at an even lower temperature at which the degradation of cotton cellulose would be held to an acceptably low level. To assure maximum reactivity, the activating effect of water on the cotton was introduced through the application of aqueous acetic acid for a short time. Its effect is almost immediate, and the minimum time of treatment for uniform activation of the goods was found to be determined by mechanical considerations in obtaining uniform saturation.

Because of the excessive swelling or gelling which the more highly substituted cellulose acetate undergoes if acetic acid is present in large quantity in the reagent mixture, it was found necessary to hold its concentration to a minimum. The best remedy was found to be the use of a nonswelling diluent which would reduce this effect. Preferably, the diluent should also have no unusually great proton affinity [9]. Thus, good circulation of the reagents would be easily maintained, and also the high activity or superacidity of the perchloric acid would not be reduced. Amyl acetate was found to be very effective in both respects, and this solvent is fortunately available in technical grades which are water-free. With this diluent present to the extent of about 50% by volume in acetic anhydride, along with 0.2% perchloric acid, cotton raw stock can be acetylated in about 2½ hr. at 15° C. (59° F.) to 42–45% acetyl content, a D.S. of 2.7 to 3.0 without difficulties due to swelling. The details of this treatment are given below in the description of a laboratory-scale method, using glass apparatus, as shown in Figure 1.

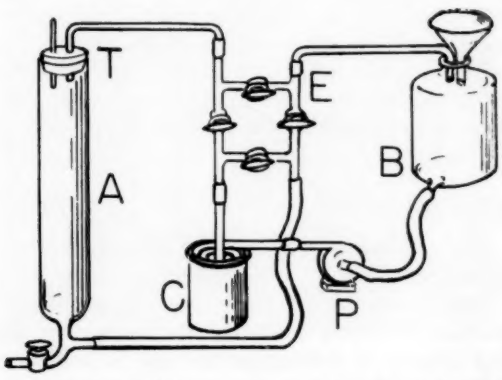

Fig. 1. Laboratory apparatus used for preparation of FA cotton.

The general similarity of the procedure and the process requirements to those of partial acetylation is fortunate in that much of the knowledge which has been gained in that development is applicable here. No unusual difficulties have been encountered in trial runs on a 6-lb. package dyeing machine which was adapted for the partial acetylation of cotton raw stock and yarn. As previously described [3], this is commercial-type stainless steel equipment adapted for acetylation by the addition of storage tanks and a small heat exchanger for cooling and removing the heat of reaction. Extra ventilation and the elimination of all leakage are required for the safety of operating personnel mainly because of the irritating and toxic effects of the acetic anhydride and amyl acetate.

The method as used on raw stock gives products of the same acetyl content when applied to scoured yarns in the form of loose skeins. However, when the yarn is held at constant length during treatment, the acetyl content falls slightly short of the full triacetate, even when the duration of treatment is nearly doubled. It appears that the physical restrictions of the yarn structure prevent the fibers from becoming completely accessible to the reaction mixture. This effect is even more apparent in the acetylation of fabric, in which additional factors of construction become involved. In general, fabrics of only 36–40% acetyl content (D.S. = 2.1 to 2.5) are produced by this method. Throughout this paper, these ranges of compositions, depending on the form of cotton treated, are collectively referred to as fully acetylated, or FA, cotton. These ranges are shown schematically along the axis of the abscissa in Figure 2.

Properties

Appearance and Handle

The appearance of FA cotton is substantially the same as that of untreated cotton, but if no softeners are applied, its handle is considerably more full, somewhat harsher, and it possesses perceptible scroop. In yarn and fabric forms, it readily responds to softening agents, and these may be used to control the harshness over a considerable range.

Increase in Weight

Upon conversion to FA cotton, the original cotton undergoes considerable increase in conditioned weight, amounting to slightly more than 50% for fully substituted stock, as shown in Figure 2. These observed increases are less than theoretical (70%, based on pure cellulose, allowing only for change in regain) because of the losses on noncellulosic constituents and parts of the cotton itself, most probably tips and fragments of lint. The increases in weight vary somewhat from sample to sample, and the line in Figure 2 gives an approximate median value.

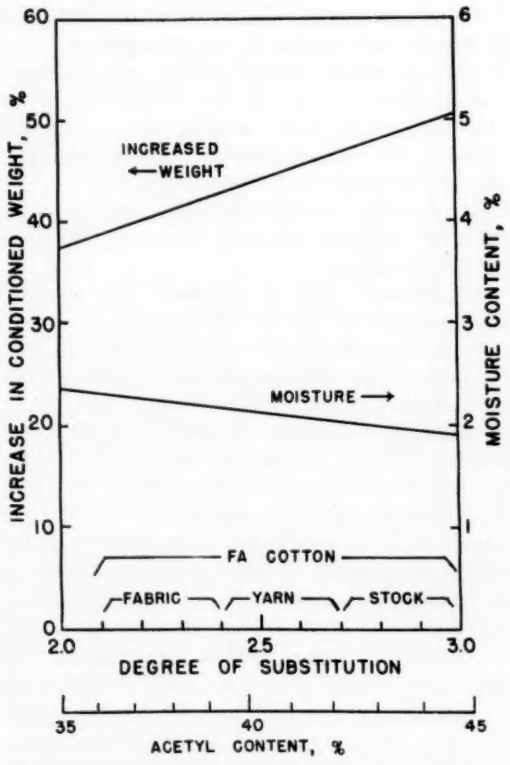

Fig. 2. Chart of relationships of moisture content and increase in weight to acetyl content of FA cotton.

Moisture Content

The moisture content of FA cotton under standard conditions ranges around 2% for the various textile forms, as shown in Figure 2. This moisture content is slightly below that of solvent-spun triacetate and suggests the possibility of quick drying characteristics. Also, comparative values of water retention on centrifuging, extrapolated to infinite speed by the methods of Welo [15] and Preston and Nimkar [12], are 30, 8.4, and 7.9% for typical untreated cotton, solvent-spun triacetate, and FA cotton stock, respectively. Taking these as a measure of swelling, the hydrophilic nature of cotton is seen to be reduced but not eliminated.

Density

The density of FA cotton ranges from about 1.33 to 1.37, as measured by the gradient column method. The values fall along the line established by Orr and co-workers [11] relating density with acetyl content for acetylated cotton. The combined effects of increase in weight and decreased density result in a calculated 75% increase in volume, though the fraction of this which may be accommodated in the lumen space has not been determined.

Degree of Polymerization and Fluidity

The D.P. of FA cotton, as measured by fluidity in cuprammonium solution, varies over the range of about 1000 to 1500. The measured fluidities are 12 to 16 rhes. at a concentration of 0.5 g. of cellulose per 100 ml. of cuprammonium hydroxide solution, with the values adjusted to a velocity gradient of 500 reciprocal seconds. Under these same conditions, scoured cottons have a fluidity of about 2.5 to 3.0 rhes. [13].

Effect of Solvents

The behavior of FA cotton stock upon exposure to various solvents is somewhat surprising when compared with that of solvent-spun triacetate, though this may be partly accounted for by its relatively high degree of polymerization. As is shown in Table I, air-dried stock (not heated in any way) is substantially unaffected by acetic acid, acetone, ani-

TABLE I. Effect of Solvents on Fully Acetylated Celluloses

Solvent	FA cotton	Solvent-spun triacetate
Acetic acid	Unaffected	Soluble
Acetone	Unaffected	Soluble
Aniline	Unaffected	Soluble
1-4 Dioxane	Unaffected	Soluble
Chloroform	Swells	Soluble
Chloroform-ethanol (90:10)	Swells	Soluble
Chloroform-ethanol (80:20)	Swells	Soluble
m-Cresol	Swells	Soluble
Formic acid	Swells	Soluble
s-Tetrachloroethane ("STE")	Swells	Soluble
STE-methanol (90:10)	Swells	Soluble

Both FA cotton and solvent-spun triacetate are unaffected by: ethyl acetate, isoamyl acetate, diethyl ether, methyl alcohol, ethyl alcohol, benzene-ethanol (50:50), carbon tetrachloride, trichloroethylene, and tetrachloroethylene.

line, and dioxane; these solvents dissolve heat-set solvent spun triacetate. Similarly, FA cotton swells but does not dissolve in formic acid, meta-cresol, chloroform, chloroform-ethanol mixtures, and sym-tetrachloroethane; all of these solvents dissolve heat-set solvent-spun triacetate almost instantly.

Electron Microscope Features

Electron microscopic examinations of FA cotton in cross section have been made. As was found with PA cotton [14], embeddings of FA cotton fibers prior to sectioning in methacrylate results in considerable cross-sectional swelling and distension frequently accompanied by separation of the cell wall. This swelling is seen in Figure 3. It was found that FA cotton does not respond as ordinary cotton to fragmentation by high speed beating in water. Electron microscopic examination, after complete saponification of FA cotton back to cellulose using dilute alcoholic sodium hydroxide, showed that the normal fibrillar organization and structure of cotton was fully retained and clearly visible, as in Figure 4. That is to say, fibrillar organization is retained throughout the steps of complete esterification followed by complete saponification.

The great stability of the cotton fibrous structure as retained by FA cotton may be demonstrated by boiling the triacetate for 2 hr. in monoethanolamine under reflux (about 165° C.). A comparison, shown in Figure 5, between FA cotton before and after this treatment with solvent-spun triacetate treated the same way shows a striking difference in stability of the structures of the different triacetates under these conditions.

Crystalline Structure

The X-ray fiber pattern of FA cotton yarn which was treated slack and had not been heated in any

Fig. 3. Cross-sectional view of FA cotton using the electron microscope. The sample was embedded in methyl methacrylate. Marks are at 1 μ.

Fig. 4. View of a fragment of completely saponified FA cotton using the electron microscope. Marks are at 1 μ.

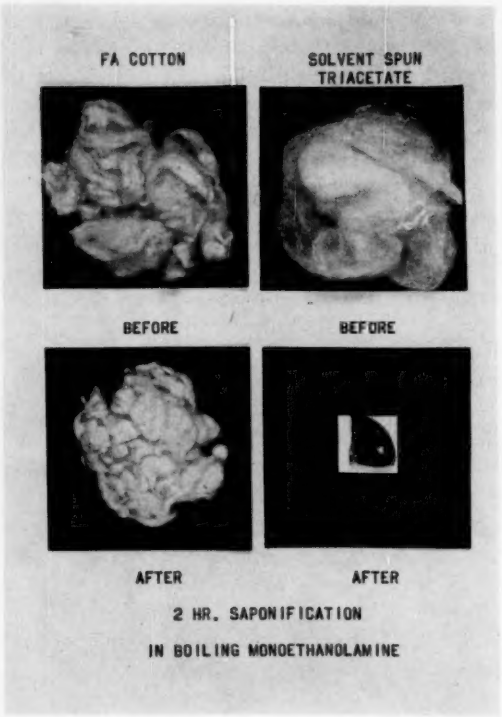

Fig. 5. FA cotton and solvent-spun triacetate before and after boiling in monoethanolamine (2 hr. at reflux).

way is shown in Figure 6. The pattern is essentially that of cellulose triacetate alone; no arcs corresponding to cellulose I remain. From the examination of only a few patterns obtained on this new product, one may conclude that the level of crystallinity is very low in comparison with that of cotton, but significantly higher than that of solvent-spun triacetate with the same thermal history. The order and orientation of the crystallites are believed to be very good.

Dyeing Properties

FA cotton can be dyed a full range of shades and colors under conditions which are common for modern dyeing practice, except that only a relatively short dyeing time is needed to meet commercial standards for exhaustion and levelness of shade. About 1 hr. at the boil, using orthophenylphenol as an accelerant or carrier and diammonium phosphate to maintain a pH of 8 gives very satisfactory results. Details of the procedure are given below.

Fiber Properties of FA Cotton Stock

The fiber properties of FA cotton stock are shown in Table II. The increase in weight fineness and decrease in bundle tenacity from the untreated cotton values are very closely in accord with those predictable from the increase in weight. The tenacity at standard conditions is about the same as that of solvent-spun triacetate. The weight fineness reported in Table II was measured with the Micronaire, using the normal cotton scale; the increases in weight fineness have also been verified using the Suter-Webb technique on a sample of Rowden cotton, which showed an increase in weight fineness from 5.70 to 8.88 μg./in. on acetylation to 44.8% acetyl content. The retention of original fiber length indicates the effectiveness of the amyl acetate diluent in preventing swelling and contraction during esterification.

The high level of retention of bundle tenacity after prolonged heating indicates that FA cotton is superior to PA cotton in heat endurance. PA cotton fiber normally loses about 20 to 35% of its bundle

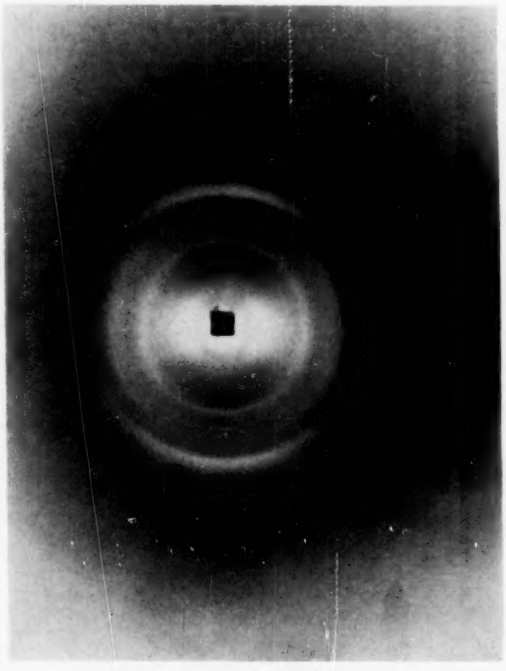

Fig. 6. X-ray fiber pattern of FA cotton, not heat treated. (Ni filtered K-alpha radiation from Cu.)

TABLE II. Fiber Properties of FA Cotton Stock

Description	Acetyl content, %	Bundle tenacity, g./den.	Bundle elongation at break,† %	Weight fineness (Micronaire), μg./in.	Upper quartile length, in.	Coefficient of variation, %
Untreated cotton*	0	2.34	10.0	4.65	1.18	28
FA cotton	44.8	1.46	9.2	6.35	1.12	33
Untreated cotton, heated 3 days‡	—	0.48	3.2	—	—	—
FA cotton, heated 3 days	—	1.24	7.3	—	—	—

* Deltapine variety. Similar results have been obtained on Pima and Rowden cottons.
† Jaw spacing 3.2 mm.; effective length 3.7 mm.
‡ At 160° C. in a laboratory oven.

TABLE III. Properties of FA Cotton Yarn

Description	Acetyl content, %	Yarn count*	Tenacity, g./den.	Strand breaking load† g.	Elong. at break† %
Untreated	0	30.2	1.13	198	5.55
Fully acetylated	40	18.7	1.19	338	6.40

* Cotton system.
† Uster Automatic Yarn Tester.

TABLE IV. Effect of Weathering on Acetylated 12/3 Cotton Yarns

Time of exposure, weeks	Breaking strength retained, %	
	17.5% acetyl	45% acetyl
4	52	64
8	35	51
12	30	45
20	23	36

tenacity in 3 days of exposure at 160° C. in a laboratory oven; FA cotton fiber loses only 15%. Heat resistance will be noted again in the discussion of FA cotton fabric properties.

Yarn Properties

A comparison of the properties of FA cotton yarn with those of the cotton yarn used in its preparation, given in Table III, shows that the chemical treatment materially increases its breaking load. The increased strength very nearly parallels the increased weight so that the count-strength product and the tenacity of the yarn remain essentially constant. These proportionate increases observed in strength and weight are in contrast to the results obtained in many other chemical treatments of cotton for which the retention of strand breaking strength is usually accepted as satisfactory.

Weathering tests on undyed FA cotton yarns show better strength retention than that of undyed PA cotton yarn, as shown in Table IV. No data on the weathering characteristics of FA cotton samples which have been vat-dyed prior to esterification are yet available.

Fabric Properties

Values of flex and flat abrasion endurance [1b], and strip breaking and trapezoid tear strength [1a], are shown in Table V for two acetylated fabrics and

TABLE V. Change in Properties on Acetylation of Cotton Fabrics

Scoured cotton sheeting	Acetyl content, %	Flat* abrasion endurance, cycles	Trapezoid tear strength, lb.	Strip† breaking strength, lb.	Flex* abrasion endurance, cycles	Elmendorf tear, lb.
48 × 48	0	128	7.6	58.4	855	5.9
Partially acetylated	13	113	4.5	49.9	151	2.3
Fully acetylated	39	405	6.7	74.2	197	2.9

* Tests conducted on the Stoll Universal Wear Tester.
† 48 warp threads.

the untreated control. The increases in strip breaking strength and flat abrasion endurance of FA cotton over the untreated control values are most striking. While the flex abrasion and Elmendorf tear strength [1c] of the FA cotton are considerably less than the original values, these tests were run on fabrics which had no softener or finish applied. More recent, incomplete trials in this direction indicate that these values can be readily doubled with selected finishes. It is interesting to note that there is an upward trend of values in going from PA to FA cotton, suggesting that service life of FA cotton might be more satisfactory than that of PA cotton in uses involving these properties. In further comparison with PA cotton, the effect of heating on fabric properties is shown graphically in Figure 7. In most of these properties, it is seen that the properties of FA cotton (39% acetyl content) after 7 days of heating at 160° C. are approximately equal to those of PA cotton (13% acetyl content) before the test heating begins.

Ironing Characteristics

The sticking temperature for FA cotton fabric under a household iron is practically the same as that for solvent-spun triacetate, about 250° C. It may be pressed with a dry household iron at the wool setting (about 200° C.) with no glazing effect. It exhibits thermoplasticity at these temperatures, and folds and pleats may be permanently pressed into the goods. These will withstand considerable mussing and even hand laundering with a neutral detergent. The pleats may then be repressed, since pressing is needed after laundering to remove wrinkles, or they may be pressed out, as desired. The pleats may be relocated with no sign of the location of the old pleat, if that is desired.

This thermoplastic nature is being evaluated in tests currently under way. Preliminary test results shown in Table VI indicate that FA cotton does not markedly change in properties under conditions of very little or no tension which are used for the heat-setting of solvent-spun triacetate. However, with the application of moderate tension for a short time while under heat, growth on cyclic loading may be reduced to extremely low values while a moderate amount of elongation-at-break is retained. Much shorter periods of heating and stressing give nearly the full effect shown in Table VI.

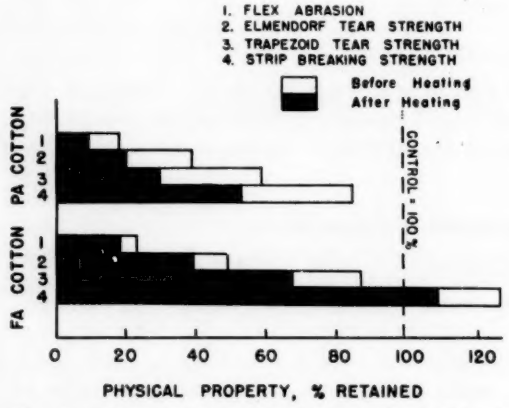

Fig. 7. Effect of heat on physical properties of PA and FA cotton.

TABLE VI. Effect of Heat and Stress on FA Cotton Fabric

Description	B.S., lb.	Elong., %	Growth,* %	Average modulus, 100 threads, lb.
Scoured cotton sheeting, 48 × 48	108	7.1	1.9	—
FA cotton sheeting	152	13.1	5.1	2940
Same, 1 min. at 200° C., no load	152	12.9	5.0	2220
Same, 34-lb. load, 1 min., no heat	154	11.8	3.7	2500
Same, 1 min. at 200° C., 34-lb. load	173	3.9	0.33	6250

* Displacement of tenth cycle hysteresis loop along elongation axis. Upper limit of loop, one-third strength.

Rot Resistance

FA cotton shows the high level of rot resistance which may be expected from its composition. Burial tests have not progressed beyond a few months, so that the level of superiority over PA cotton has not yet been shown. Test results should be available in one or two years.

Laboratory Preparation of FA Cotton

Apparatus of the type shown in Figure 1 may be conveniently used in the laboratory for acetylation of raw stock, yarn in skein form, or fabric. The cotton is loosely arranged in the reaction cylinder, activated for 10 to 30 min. in a mixture of acetic acid and water containing 20% of the latter by

volume. The volume:weight ratio for the apparatus shown is about 25:1. After draining, the cotton is given two 10-min. exchanges with glacial acetic acid, to the first of which is added sufficient acetic anhydride to react with the water retained by the fabric. The acetylating reagent solution, containing 1 part catalyst solution (4% perchloric acid in glacial acetic acid) and 19 parts of a solution of 50% by volume acetic anhydride in amyl acetate is circulated through the cooling coil while by-passing the reaction cylinder until 15° C. is reached. The solution is then pumped through the reaction cylinder containing the activated cotton. The reaction is allowed to proceed for 2½ hr. at 15° C., during which time the direction of flow is reversed periodically. The catalyst is neutralized by adding about threefold stochiometric excess of potassium acetate (1 part of 12% potassium acetate in glacial acetic acid) dissolved in acetic acid to the acetylation solution. After draining, the product is washed until free of odor and dried. In the laboratory, the use of ethyl alcohol materially hastens the removal of amyl acetate.

The acetyl content of the products is readily determined by the Eberstadt method as modified by Genung and Mallatt [7].

Dyeing Procedure for FA Cotton Using Disperse (Acetate) Dyes

Materials used	
Diammonium phosphate	6 lb./100 gal. water
Dowicide A*	6 lb./100 gal. water
Sodium hydroxide	2 lb. to dissolve Dowicide A
Duponol G*	2 lb./100 gal. water
Acetate dyestuff	As required (OWF)
Igepon T-51*	0.5% (OWF)

* The mention of trade names does not imply endorsement of products by the Department of Agriculture over similar products not mentioned.

Procedure

Set bath at room temperature with diammonium phosphate and work fabric for 10 min. Add one-half of the previously dissolved Dowicide A and continue to work fabric in this solution for 10 min. longer at room temperature. Add the remaining Dowicide A and slowly raise temperature to 130° F. (approximately 8–10 min.); then add Duponol G and run fabric at this temperature for 10 min. Add the dispersed, diluted, and filtered dyestuff to the bath exercising caution not to let the dyestuff come in immediate direct contact with the fabric. Run fabric for 2–3 min., raise temperature to the boil, and dye for 1 hr. The fabric is then washed with hot water for 5 min., and given a light scour for 15 min. at 140° F. with 0.5% Igepon T-51 (OWF) and 10.0% diammonium phosphate (OWF). One warm rinse (140° F.) and two cold rinses (5 min. each) complete the procedure.

Summary

Fully acetylated cotton (FA cotton), a chemically modified fiber made from cotton and retaining its fibrous form, has been made by a method which promises to be feasible commercially. The product has good tenacity in yarn and fabric forms, low moisture regain, ready dyeability, and does not require unusual care in ironing. It has the desirable properties of resistance to heat and rot, together with more abrasion resistance and tear strength than PA cotton, which is finding limited commercial application. It has some thermoplasticity and the range of elastic properties which can be obtained by the combined application of heat and stress is considerable. Although these evalutions have been conducted on a limited exploratory basis, collectively they give exciting promise of a chemically modified cotton which has many features which are sought in "new" fibers.

Acknowledgment

The authors wish to express their gratitude to a number of specialists who have contributed greatly in the rapid and fruitful examination of this chemically modified cotton and interpretation of their findings; Mary Rollins and Verne Tripp for the light and electron microscope studies, Dr. Leon Segal for the X-ray diffraction patterns, Milton Hoffman for the dyeings and John D. Tallant for the tests of elastic properties.

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Preliminary Report on Service Uses of Cyanoethylated Cotton Products[1]

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IN previous publications the mechanism of the reaction of acrylonitrile with cotton [1, 5, 6, 8, 10, 11, 12] and several methods for the production of cyanoethylated cotton products of commercial interest has been described [2, 5, 6, 7, 11]. During the summer of 1956 the Azoton Pilot Plant, designed and installed by the American Cyanamid Company and located at the National Plant of Standard-Coosa-Thatcher Company, Rossville, Ga., was used to produce 2500 lb. of cyanoethylated cotton fiber and yarn, thus bringing the total amount produced in this unit to about 20,000 lb. [5, 6]. This cyanoethylated cotton fiber and yarn, together with the 18,000 yd. of cyanoethylated cotton fabrics produced in the semiworks cyanoethylation unit at Monsanto Chemical Company, Texas City, Tex., has been placed largely into a market evaluation program. Reports from about 30% of the cyanoethylated products put into service uses have thus far been made. Some of these have been very encouraging, whereas others have reported that the products did not give the expected performance.

Market Potential of Cyanoethylated Cotton Products

In a joint report by American Cyanamid Company, Monsanto Chemical Company, and the Institute [7], the improved properties of cyanoethylated cotton compared with cotton are enumerated and include: permanently rot- and mildew-proof, more resistant to wet and dry heat degradation, more resistant to degradation by organic and mineral acids, lower moisture regain, altered dyeing characteristics, different stress-strain fiber properties, and altered electrical properties. Using these properties as a basis for a market evaluation program, the proposed end uses in relation to these properties are summarized in Table I. Some idea of the market potential of cyanoethylated cotton products, should its properties prove superior to those of cotton in service uses, may be gained from a study of the report of the National Cotton Council in 1955 [13]. Data pertinent to the present problem have been extracted and are shown in Tables II and III. It will be noted that the total potential is over one million bales of cotton annually. Even if only a part of this cotton market was diverted to cyanoethylated cotton, it would be sizeable. It should also be mentioned that that part of the cotton market gained by cyanoethylated cotton is not actually lost to cotton, but rather this becomes a part of the market for cotton. In view of the continuing losses of the cotton market to synthetic fibers, the development of a new fiber material derived from cotton is of importance to a large segment of the population that depend on the consumption of cotton for a livelihood.

[1] Azoton registered trademark for cyanoethylated cotton, Institute of Textile Technology.

TABLE I. Uses of Cyanoethylated Cotton According to Properties Which Should Result in Improved Performance

Mildew- and Rot-Resistant

Sewing thread	Filter fabric
Seed bed covers	Awning
Tobacco shade cloth	Tents
Tarpaulins	Outdoor furniture
Auto deck and seat covers	Irrigation dams and tubing
Paper makers' felts	Tennis net twine and rope
Sheeting	Tent rope
Fire hose and other hose	Towels
Outdoor wearing apparel	Seed sacks
Shelter halves	Household goods
Shoe lining	Fish lines and nets

Acid Resistant

Sewing thread	Sacks-fertilizer
Filter cloth	Awning
Fire hose	Tarpaulin
Conveyor belts	Towels
Fender fabric	Paper makers' felts
Wearing apparel (Lab coats, etc.)	Pottery clay
	Filters

Heat Resistant

Laundry press covers	Tire cord
Enameling duck	Fire hose
V-belts	Abrasive fabrics
Conveyor belts	Laundry padding
Paper makers' felts	Chafer fabric
Industrial dust filters	

Abrasion Resistant

Abrasives	Shade cloth
Buffer wheel fabric	Sewing thread
Wearing apparel (knitted and woven goods)	Rugs
	Shoe uppers
Sacks and bags	Shoelaces
Paper makers' felts	Bookbinding
Webbing	Hose
Tapes	Towels
Socks	

Electrical Insulation

Thread
Fabrics

Strength

For all items except insulation and padding

Dyeing

Apparel, knit and woven fabrics dye effects
Sewing thread
Twine, cord, acid dyes
Socks

TABLE II. Estimated Cotton Consumption for Various End Uses in Which Cyanoethylated Cotton Performed Satisfactorily

End use		Number of bales
Fish net and lines		30,300
Fish lines	830	
Netting	10,150	
Seine twine	19,320	
Marine ropes		No data
Sand bags (1953 consumption, 500 bales)		10
Filter fabrics		12,000
Seed bed covers		5,180
Tobacco shade cloth		3,780
Rugs		246,700
Abrasive fabrics (buffing wheels)		13,260
Chafer fabrics (machine belts)		67,410
Laundry press covers		67,260
Apron duck	9,790	
Cover cloth	14,140	
Press material	43,330	
Twine (industrial thread)		137,640
Tarpaulins and awnings		121,880
Tarpaulins	62,550	
Awnings	59,330	
Insulating yarn		106,450
Knit goods		Difficult to estimate, but large market
Sutures		No data, but small market
Enameling duck		No data
Hose		39,680
Fire	18,560	
Other	21,120	
		851,550 bales (500 lb. each)

TABLE III. Other Industrial Uses That Could Provide a Market for Cyanoethylated Cotton

End use	Number of bales
Bags (fertilizer)	6,940
Flags	2,720
Friction tape	8,880
Luggage lining	4,240
Mailbags	2,460
Paper makers' felt	8,840
Pick sacks	15,340
Shoes	147,560
Tents	54,670
Wiping cloth	27,460
	278,660 bales (500 lb. each)

Some Market Evaluation Results

1. *Mildew- and Rot-Resistant*

Cyanoethylated Cotton Fish Lines and Nets. Tests were made by A. von Brandt [14] on 50/15 metric number ply yarn designated as No. 6 thread cyanoethylated at the Institute to nitrogen contents of 3.4, 5.4, and 6.7%. In these tests, the yarns were submerged in the Elbe River Estuary for a total time of 42 weeks. Samples were taken for wet breaking strength tests at various time intervals. The results obtained are summarized in Table IV. It will be noted that the cotton twine had completely deteriorated after 4 weeks, whereas as cyanoethylated twine had lost no strength after 42 weeks, i.e., from April 1, 1955 to January 15, 1956.

TABLE IV. Effect of the Time of Exposure of Cyanoethylated Cotton Fishing Twine in the Elbe River Estuary on the Wet Breaking Strength, in Kilograms

Time, weeks	Avg. temp., ° C.	Intensity of attack	% Nitrogen			
			0	3.4	5.4	6.7
0	6.1	2	7.4	6.5	6.5	6.5
4	10.2	82	0	6.2	6.9	6.3
8	14.0	90		5.7	7.0	6.5
12	18.9	100		—	—	—
16	19.7	100		—	—	—
22	17.8	98		6.4	6.5	6.4
31	12.1	43		—	—	6.4
40	6.9	35		—	7.5	—
42	4.2	—		5.7	7.0	6.5

Attention is called to the column heading "Intensity of attack," Table IV. This index is the percentage loss in wet tensile strength of an untreated 50/15 cotton twine at the end of 14 days exposure. It will be observed that this index is high when the temperature of the water is high, as might be expected.

It will also be noted that cyanoethylated cotton twine with a nitrogen content of 3.4% showed about the same immunity to microbiological attack as the twine containing 5.4 and 6.7% nitrogen. There is thus no advantage to be gained in cyanoethylating to the higher nitrogen contents in this particular use.

In another series of tests on a cyanoethylated six-thread medium twine, 8.23 finished yarn size with a nitrogen content of 3.4%, it was found that in addition to the twine losing no strength in soil burial tests it only lost about 15% as much wet knot strength as cotton and had essentially equivalent abrasion resistance and only slightly increased elongation.

Finished cotton fish nets may also be cyanoethylated. Nets constructed of 20/9 and 10/18 cyanoethylated cotton twine were evaluated in service. The former twine was used to construct a 1½-in. mesh net and the latter a 2¼-in. mesh net. The cyanoethylated cotton nets appeared to be somewhat stiffer than similar cotton nets, but this was considered an advantage to the user. The net constructed of 20/9 cyanoethylated twine was considered better than that constructed of 10/18 cyanoethylated twine, but both were very much better than cotton nets of similar constructions in service tests. Some of the twine from the cyanoethylated cotton nets was unknotted and placed in soil burial tests. No evidence was found that the twine deteriorated at the spots where there had been a knot, thus indicating uniformity of cyanoethylation throughout the knots. Knot slippage in the cyanoethylated cotton nets was also found to be higher than for cotton.

Cyanoethylated Marine Rope. Cotton yarn cyanoethylated to a nitrogen content of 3.8% was plied to make a marine rope ¼ in. in diameter. Five strands of this rope, along with similar groups of acetylated cotton, copper naphthenate treated cotton (1.8% Cu), manila, cyanoethylated manila, copper naphthenate (0.15% Cu)–G-4 (0.15%) treated manila and nylon ropes, was mounted in special racks and partially submerged in a fresh water reservoir, Figure 1. The appearance of one of the racks

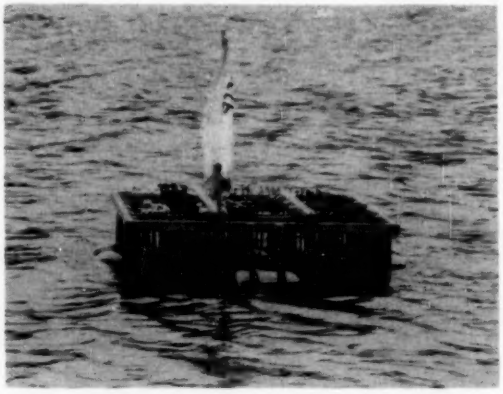

Fig. 1. Marine rope fresh water reservoir test. Courtesy of Corps of Engineers, U.S. Army, Engineer Research and Development Laboratories, Fort Belvoir, Va.

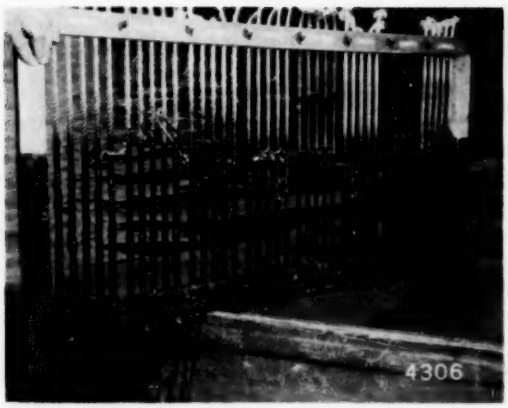

Fig. 2. Appearance of marine ropes after partial submersion in fresh water reservoir for 23 weeks. Reading from left to right in groups of five strands, the treatments are: cotton, acetylated cotton, cyanoethylated cotton, copper naphthenate-treated cotton (1.8% Cu), manila, cyanoethylated manila, copper naphthenate-G-4 treated manila and nylon. Courtesy of Corps of Engineers, U.S. Army, Engineer Research and Development Laboratories, Fort Belvoir, Va.

after 23 weeks is shown in Figure 2. Upon testing for breaking strength the results given in Table V were obtained. It will be noted that the cyanoethylated cotton rope had gained 15% in strength, whereas the cotton rope had lost 68%. Acetylated cotton rope lost no strength, and rope treated with the mildewcide copper naphthenate to a copper content of 1.8% had gained 14% in strength. Of some interest also is the performance of cyanoethylated manila rope with relation to untreated manila and manila rope treated with a copper naphthenate–G-4 mixture. This test will be continued until strength losses in the special ropes occur.

Cyanoethylated Sewing Twine in Outdoor Use. Comparative weathering tests were made on 12/4 cyanoethylated cotton, cotton, and phenyl mercuric salicylate (0.01%) treated cotton sewing twine. The twine samples were all exposed to full Georgia sun during the summer months. Samples were tested for tensile strength at various intervals of time wtih the results obtained shown in Table VI.

Seam tests made on cotton duck sewn with cyanoethylated cotton, Dowicide treated cotton, and Orlon,[2] sewing twine after 14 weeks outdoor weathering showed that the cyanoethylated cotton twine seam was equal to or better than, the proofed cotton twine seam, and both were better than the Orlon twine seam, Table VII. It will be noted that the predominant type of seam failure for the Orlon twine seam was fabric failure at the stitch due to cutting, whereas fewer of the seam failures were of this type on the proofed and chemically modified

TABLE V. Fresh Water Reservoir Submersion Tests on ¼-in. Diameter Marine Rope Constructed of Various Types of Chemically Treated and Modified Cotton and Manila

Cotton product	Breaking strength		
	Orig.	After 23 weeks	% Loss
Untreated	441	138	68
Acetylated	312	312	0
Azoton	468	540	15 (gain)
Proofed cotton*	345	394	14 (gain)
Manila	596	160	73
Cyanoethylated manila	518	536	3 (gain)
Proofed manila**	615	407	3
Nylon	not tested		

* Copper naphthenate (1.8% Cu).
** Copper naphthenate (0.15% Cu)–G-4 (0.15%).

TABLE VI. Weathering Test on 12/4 Cyanoethylated Sewing Twine and Mercury-Treated Cotton Twine

Time, weeks	Breaking strength, lb.		
	Untreated	Azoton	Mercury*
0	6.9	7.9	6.9
4	6.4	7.7	5.8
9	5.1	6.9	4.4
14	3.8	5.2	3.6

* 0.01% Phenyl mercuric salicylate.

TABLE VII. Seam Tests on Duck Sewn with Various Types of Thread after 14-Weeks Exposure

12/4

Azoton, lb.		Proofed cotton,* lb.		Orlon, lb.	
Orig.	Exp.	Orig.	Exp.	Orig.	Exp.
154T**	122T	137S	132T	125S	114S
142S	130S	130S	116S	119S	110S
142T&S	125S	112S	118T	122S	110S
117T	130S	116T&S	121T	109S	105S
127T	134T	146T	132F	100S	110S
123T	110S	150T	118F	103S	118S
	132S		130T		110S
	122S		130S		110S

* Dowicide G.
** T, twine failure; S, fabric failure at stitch; F, fabric failure away from seam.

[2] Du Pont acrylic fiber.

cotton twine seams. The seam failures of both of the latter yarns were largely twine failures and these were at a definitely higher level than the failures at the seam when Orlon twine was used. It will be noted also that the fabric breaking strengths at the stitch for the cyanoethylated and proofed cotton twine seams were at a higher level than those sewn with the Orlon twine.

Cyanoethylated Cotton Tobacco Shade Cloth. Cyanoethylated cotton tobacco shade cloth was put into several service tests in Florida. The breaking strengths of the cyanoethylated cotton shade cloths after exposure for one season, in two of these tests, are shown in Table VIII. It will be noted that the cyanoethylation of the cotton shade cloth decreased the original breaking strength in the warp from 21.7 to 16.6 lb. but increased the strength of the filling from 20.2 to 27.4 lb. In Test No. 1 the average losses in strength of the fabrics in the warp- and filling-wise directions were 60% for cotton and only 37% for the cyanoethylated cotton after one season's exposure. In Test No. 2 these losses were 74.1 and 7.8%, respectively.

In other tests cyanoethylated cotton tobacco and seed bed cover fabric lost more strength than cotton during service use. A partial explanation for this may lie in the fact that in most of these instances the fabrics were kiered and bleached prior to cyanoethylation, whereas in the above-cited examples greige fabric was cyanoethylated. At the present time, studies are underway with the objective of determining the cause for the poor weatherability of some cyanoethylated cotton fabrics and with the development of treatments to minimize deterioration in outdoor uses.

2. *Acid Resistance*

Filter Fabric. In comparative tests with 8-oz. cotton filter twill, cyanoethylated cotton fabric was found to give three to four times longer service, Table IX. In this instance a hot mineral acid solution was filtered.

Tests similar to those earlier reported showing the acid resistance of cyanoethylated cotton fabric were made on an 8.8-oz. cyanoethylated cotton twill fabric containing 3.35% nitrogen. In this test a 40% sulphuric acid solution was used at 75° F. After standing in the acid solution for 24 hr. the cotton and cyanoethylated cotton fabrics were removed, neutralized, rinsed, dried, and after conditioning, 1-in. raveled strip breaking strength determinations made in the warp- and filling-wise directions. The results obtained, expressed in percentage breaking strength loss, are given in Table X. This experiment was repeated after washing both the cotton and cyanoethylated cotton in a commercial home laundry machine. It will be noted that the average loss in strength after washing the cotton was less than before washing, whereas the reverse was true for cyanoethylated cotton. The effect of prewashing the fabrics may be of no significance, but the lower loss in strength experienced by the cyanoethylated cotton is real.

3. *Heat Resistance*

Laundry Press Cover Fabric. A large number of service tests were conducted in commercial laundries using cyanoethylated cotton fabric (3.5 to 4.0% nitrogen) in place of cotton on both ironer rolls and presses. A large number of variables enter into such a full-scale service evaluation, which will not

TABLE VIII. Cyanoethylated Cotton in Tobacco Shade Cloth

	Breaking strength, lb.			
	Cotton		Azoton	
	Warp	Fill	Warp	Fill
Original	21.7	20.2	16.6	27.4
Field Test No. 1*	7.9	6.4	11.6	16.1
Field Test No. 2*	5.6	5.2	15.4	21.2

* One-season exposure in Florida.

TABLE IX. Cyanoethylated Cotton Filter Twill for Filtering an Acid Solution at 120° F.

Product	Average life, hr.
Cotton	24
Azoton	72 to 96

TABLE X. Cyanoethylated Cotton Fabric for Overalls, 8.8-oz. Twill 3.35% N

(% Loss in tensile strength after 24 hr. in 40% H_2SO_4*)

Original		Washed	
Cotton	Azoton	Cotton	Azoton
70(W)	46(W)	67(W)	55(W)
80(F)	56(F)	73(F)	53(F)

* Temperature 75° F.

be mentioned here. The data summarized in Table XI are sufficient to show the superior performance of cyanoethylated cotton press fabrics with relation to similar cotton fabrics in this case. More complete details concerning the tests can be furnished those interested.

Comparative tests of cyanoethylated cotton fabric were also made with nylon and Dacron [3] laundry press fabric. From these service tests it was possible to determine the relative cost of using cotton, cyanoethylated cotton and nylon or Dacron fabric. The data shown in Table XII are based on the cost of cyanoethylated cotton fabric (7.25 oz./ sq. yd.) being 20¢ per yard greater than for a similar cotton fabric. This is, of course, only an approximation based on pilot plant studies [7].

It would appear that on a cost-per-day basis cyanoethylated cotton press fabric could easily gain favor in laundry use. However, in the service tests it was found that the sticking of starched goods to cyanoethylated cotton press cloths was as great as to cotton. This resulted in a buildup of starch on these covers so that it was necessary to wash them after a week or 10 days use, whereas this was not found to be the case for nylon and Dacron covers. The labor required for removing and replacing the covers after washing, together with the laundering of the covers, reduced the savings resulting from the lower initial cost to a point where it was questionable that the cyanoethylated cotton press cloth was the better buy. It is possible that laundry press covers produced from cyanoethylated cotton fabric with a nitrogen content in the range of 4.5 to 5.0% would give longer life in service than those used in the tests described. If this is found to be the case, there is little doubt that this product would be favored by commercial laundries over both cotton and nylon or Dacron press covers.

In laundry roll covers the service life of 29 oz./yd. cyanoethylated cotton fabrics was found to be about one third that of the Dacron fabrics ordinarily used. In this case, however, the cost of the Dacron fabric was $5.60 per square yard, whereas the cyanoethylated cotton fabric was estimated to be $1.90. It is thus evident that cyanoethylated cotton roll covers are competitive with Dacron covers.

Enameling Duck. Cyanoethylated cotton enameling duck, 37 × 45, 9.2 oz./sq. yd., was put into a typical fabric coating use where it was subjected to a temperature of 195° F. for a period of 6 weeks. It will be noted in Table XIII that the losses in both tensile strength and tear strength were considerably less for the cyanoethylated cotton fabric than for the cotton fabric. Particularly outstanding are the low tearing strength losses.

When the enameling ducks were given a preshrinking treatment of the sanforizing type prior to service use, the results shown in Table XIV were obtained for tensile and tear strength in both the warp and filling directions.

It will be seen that tensile strength loss of both the

TABLE XI. Cyanoethylated Cotton Laundry Press Fabrics

Test No.	Type work	Average life, days: Cotton	Azoton
1	Towels, aprons	10–15	22–27
2	Aprons	15–20	24
3	Sheets	25–30	55
4	Cases, towels	10 and less	22
5	Family flat	15	20
6	Family flat	15	30

TABLE XII. Comparative Cost of Cyanoethylated Laundry Press Fabrics with Other Press Fabrics

Fabric	Average use, days	Cost per yd.	Cost per day, cents
Cotton	15	$1.00	5.5
Azoton	30	1.20	4.0
Nylon	50	3.65	7.3

[3] Du Pont polyester fiber.

TABLE XIII. Loss in Tensile and Tear Strength of Cotton and Cyanoethylated Cotton Enameling Duck After 6 Weeks Service Use at 195° F.

(37 × 45, 9.20-oz. duck)

Product	% Loss tensile strength	% Loss tear strength
Cotton	24.2(W)	42.4(W)
	16.7(F)	32.0(F)
Azoton	16.8(W)	8.2(W)
	11.4(F)	0.0(F)

TABLE XIV. Loss in Tensile and Tear Strength of Preshrunk Cotton and Cyanoethylated Cotton Enameling Duck after 6 Weeks Service Use at 195° F.

Product	% Loss breaking strength	% Loss tear strength
Cotton	11.2(W)	65.6(W)
	15.0(F)	45.1(F)
Azoton	6.6(W)	10.0(W)
	15.6(F)	14.6(F)

cotton and cyanoethylated cotton was less after preshrinking except for the latter in the filling-wise directions, whereas the tear strength loss was greater for both the cotton and cyanoethylated cotton fabrics. Again, however, the latter fabric was found to have deteriorated to a lesser extent in service, as determined by the the tensile and tear strength losses, than the former fabric.

Conveyor Belt Duck. It was proposed to put a rubber conveyor belt reinforced with 28-oz. cyanoethylated cotton duck into a high temperature service use and compare the performance with a similar belt reinforced with cotton duck. Breaking strength tests were thus made on the 7.5/3 cotton and cyanoethylated cotton yarn after treating under simulated service conditions as follows: (*a*) after 15 hr. at 320° F.; (*b*) after heating for 4 hr. at 220° F.; (*c*) fully wet out, and the per cent change in strength calculated with relation to the tensile strength of the yarns conditioned at 65% RH and 72° F. The effect of weaving the 7.5/3 yarns into the 28-oz. fabrics was also determined for each of these properties by removing the yarns from the woven fabrics. The results obtained are shown in Table XV.

It will be noted that both the cotton and cyanoethylated cotton were apparently damaged as a result of weaving, although the relationship between the two types of fibers after subjecting to various tests was essentially unchanged. The heating of the yarns at 320° F. for 15 hr. caused a loss in strength of the cotton (34.5%) about six times as great as for the cyanoethylated cotton (6.7%) after reconditioning at 65% RH and 72° F.; whereas heating for 4 hr. at 220° F. and testing immediately, cotton (26.4%) lost about five times as much strength as cyanoethylated cotton (5.4%). When the yarns were fully wet out and tested for tensile strength, the cotton (20.0%) increased in strength to a lesser extent than the cyanoethylated cotton yarn (29.0%).

In tests made on the fabric it was found that the breaking strength of the 28-oz. cyanoethylated cotton duck was 10% lower than for 28-oz. cotton duck. When heated for 4 hr. at 220° F., however, the former fabric was 10% stronger than the latter. Since the fabric is cured in rubber in a dry condition, the cyanoethylated cotton duck should produce initially a stronger conveyor belt than cotton duck of the same weight and retain this strength under high temperature use conditions for a longer time.

4. *Abrasion Resistance*

In some service uses the abrasion resistance of cyanoethylated cotton fabric has been found to be greater than that of cotton fabric [2, 3, 4, 5], whereas in other uses the reverse is true. An example of the former is shown in the case of cyanoethylated cotton chafer fabric used in V-belt covers.

V-Belt Cover Fabric. Cyanoethylated cotton chafer fabrics with nitrogen contents of 2.65 and 3.85%, along with cotton chafer fabric, were used as covers for V-belts and placed in accelerated service tests. Each test consisted of four belts each. The average time to failure of each series of belt covers was determined, Table XVI. The outstanding performance of cyanoethylated cotton chafer fabric with a nitrogen content of 3.85% will be noted although

TABLE XV. Change in Single End Breaking Strength of 7.5/3 Yarn Taken from 28-Oz. Cotton and Cyanoethylated Cotton Conveyor Belts under Various Conditions Following Testing at 65% RH and 72° F.

Test No.*	Before weaving		After weaving	
	Cotton	Azoton	Cotton	Azoton
1	−34.5	−6.7	−39.6	−3.6
2	−26.4	−5.4	−28.8	−10.6
3	+20.0	+29.0	+26.9	+18.1

* (1) After 15 hr. at 320° F. followed by reconditioning, (2) Bone dry, (3) Fully wet.

TABLE XVI. Cyanoethylated Cotton Chafer Fabric in V-Belt Covers

Product	Belt cover failure, hr.*
Cotton	139
Azoton (2.65% N)	195
Azoton (3.85% N)	234

* Average of 4 test belts.

TABLE XVII. Electrical Insulating Properties of Cyanoethylated Cotton Fabric

Fabric	Resistivity, ohms	
	Room conditions	40° F.; 95% RH
Cotton	9.1×10^{11}(W) 1.1×10^{12}(F)	8.7×10^{6}(W) 8.1×10^{8}(F)
Azoton	1.1×10^{13}(W)* 1.1×10^{13}(F)**	6.5×10^{7}(W) 4.7×10^{7}(F)

* (W) Warp 3.8% N.
** (F) Filling 3.1% N.

even with a nitrogen content of 2.65% greater life was experienced. It should be pointed out that an optimum nitrogen content for each fabric use may eventually be found, but in this preliminary survey it was necessary to limit the number investigated.

5. *Changed Electrical Properties*

Cyanoethylated cotton fabric (80 × 80 print cloth) has been found to have better insulating properties than cotton, Table XVII. The cotton and cyanoethylated cotton fabrics were tested under normal room conditions and at 95% RH and 140° F. for resistivity. The results from service tests indicate that the insulating and resistance to heat deterioration properties are not, however, sufficiently better than cotton to warrant the added cost of production in some uses. In other uses this is not necessarily the case.

6. *Yarn Manufacture from Cyanoethylated Cotton Fiber*

In previous publications it has been pointed out that bulk cotton could be cyanoethylated successfully, [5, 6, 7]. In order to process cyanoethylated cotton fiber on the conventional cotton processing system, it is necessary to apply a softener in the last rinse water following cyanoethylation. A suitable softener has been found to be Ahcovel-F which is applied from a 2% solution based on the weight of the cyanoethylated cotton. An even better aid to processing this new fiber material is a mixture of 2% Ahcovel-F and 0.11% Ucon Oil HB2000 applied from a water dispersion based on the weight of the cyanoethylated cotton fiber. The softened cyanoethylated cotton fiber can be made into a picker lap using the finisher section of a picker, and is then carded to produce a 55-grain sliver. After two processes of drawing, it may then be processed into a 1.0 H.K. roving, and this roving into a nominal 22/1 yarn. The physical properties of the yarns produced in this manner, along with those of a cotton yarn of the same count, are shown in Table XVIII.

TABLE XVIII. The Effect of 2% Ahcovel-F Softener with and without 0.11% Ucon Oil HB2000 on the Physical Properties of Azoton Cotton Yarn, 3.7% Nitrogen

Treatment	Yarn No.	Single end breaking strength			% NU
		Grams	Grams/ grex	Per cent Elong.	
Cotton	22.6/1	435	1.67	7.5	101.5
Azoton + Softener	21.4/1	378	1.37	5.3	177.5
	21.4/1	392	1.42	5.6	173.0
Azoton + Softener + Oil	23.2/1	330	1.30	5.7	140.8
	23.1/1	344	1.34	5.9	150.2

It will be noted the addition of the Ucon Oil to the Ahcovel-F softener caused a decrease in yarn strength but an improvement in yarn uniformity. In general the strength of the cyanoethylated cotton yarn with relation to cotton yarn is decreased in proportion to the number of fibers in the yarn cross sections. Since cyanoethylation to a nitrogen content of 3.7% increases the fiber weight by about 15%, the number of fibers in the yarn cross section will be decreased by this amount. Since the strength of the individual fibers is not changed by cyanoethylation, it should follow that the strength of the yarn should also decrease 15%, all other factors remaining the same. This in general has been found to be the case. Further work is needed on fiber finishes, and processing procedures before a high quality yarn can be produced from cyanoethylated cotton fiber.

Other Uses. Some of the other uses in which cyanoethylated cotton products have been evaluated are given in the Summary of the Market Evaluation Program along with some of the conclusions drawn, Table XIX.

Cost of Cyanoethylating Cotton

In the joint report issued by the Institute, American Cyanamid Company, and Monsanto Chemical Company [7] detailed procedures are described for the cyanoethylation of cotton which can serve as the basis for large-scale development for both batch and continuous operations. A flow sheet of a projected batch process for a plant producing 6 million lb. of cyanoethylated fiber or yarn annually, to cost $300,000 to $375,000 exclusive of a building, winding facilities, and warehouses, is shown in Figure 3. In Figure 4 a flow sheet of a continuous process for cyanoethylating cotton fabric in open width is shown. This plant, costing about $275,000 to $325,000 exclusive of building, steam, and warehouse would have an annual production of about 11 million lb. The batch process can best be carried out in package dyeing equipment in which cotton is treated in a single operation with acrylonitrile and caustic soda

TABLE XIX. Azoton Market Survey

No.	Item	Report
1	Fish net and lines	Excellent, large demand.
2	Marine ropes	No strength loss after 1 year. Test continuing.
3	Sand bags	Good after 2 years. Cotton deteriorated in 1 month.
4	Filter fabrics	Two to three times better than cotton where heat and acid are used.
5	Seed bed covers and Tobacco shade cloth	Good performance when in contact with ground or used on side walls as shade cloth.
6	Rugs	Firmer hand than cotton. Washed clean easier.
7	Abrasive fabrics	Excellent performance (three to four times better). Electroplating polishing, large market. Other users found it inferior to cotton.
8	Chafer fabric	Three to four times longer life in V-belt covers. In some other rubber items performance not good.
9	Laundry press covers	Two to four times longer life than cotton. Most launderies prefer Dacron and nylon covers.
10	Twine	Sewing twine, excellent performance in tarpaulins.
11	Thread	Favored over Cu-8 treated cotton. No dermititis, sews well. Improvements in wearing apparel over cotton not sufficient to warrant change in most uses it is claimed.
12	Tarpaulins and awnings	Tests not complete. Good thus far. Demand for goods.
13	Insulating yarns	Good in tropics where mildew is a problem. Cannot compete with glass yarns and fabrics in high temperature motors.
14	Knit goods	No difficulty in knitting. Some unlevel dyeing encountered.
15	Sutures	Encouraging performance. Good knot strength.
16	Mops	Longer wear, faster absorption rate.
17	Corduroy	Difficulty in weaving and cutting. Softener application necessary. Prospects not too encouraging.
18	Reinforcing premolded rubber goods	Excellent performance.
19	Enameling duck	Excellent, three to four times better than cotton.
20	Hose	Preliminary tests indicate use in forest fire hose.

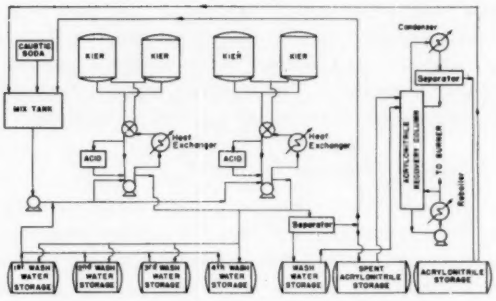

Fig. 3. Flow sheet for the batch cyanoethylation of cotton.

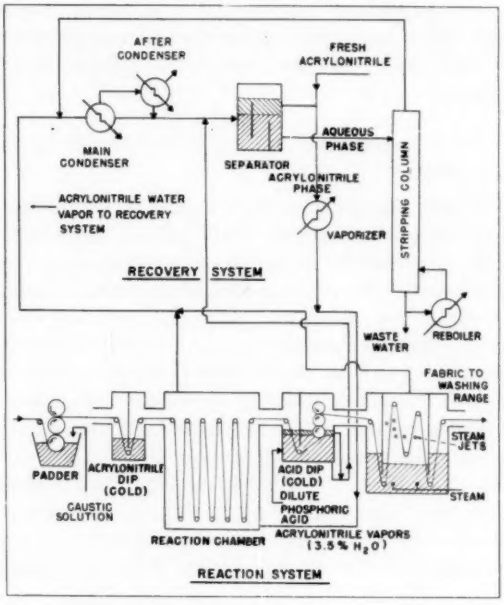

Fig. 4. Flow diagram for continuous open-width cyanoethylation of cotton fabric.

solution, whereas the continuous process consists of padding on caustic soda solution followed by contact with acrylonitrile vapor. Production costs by either method on fiber, yarn, or fabric is estimated to be 13 to 16¢ per pound.

Conclusion

Certain properties of cotton are changed by cyanoethylation so that improved performance in service uses, where rot and mildew, high temperature and acid conditions prevail, is realized. Other properties

of cyanoethylated cotton differing from cotton that may prove of economic importance include: altered dyeing characteristics [9]; lower moisture regain; increase in electrical insulation, flat abrasion resistance, and work required for rupture under tension.

End uses where these properties have been found useful include: fish nets and lines, marine rope and throngs, webbing, sand bags, tobacco shade cloth, seed bed covers, enameling duck, acid filter cloth, sewing twine, sewing thread, tarpaulins, awning, electrical wire insulation for tropical use, chafer fabric for V-belt covers, buff wheel fabric, vulcanized fiber reinforcing, premolded rubber goods reinforcing, household ironing-board covers, special-use laundry press and roll covers and special fire hoses. Data obtained in a market evaluation program on cyanoethylated cotton items has been presented for some of these.

The cost of producing cyanoethylated cotton fiber, yarn and fabric by either a batch or continuous process, as determined from pilot plant studies, is estimated to be 13 to 16¢ per pound.

Acknowledgment

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The interest and enthusiasm of the Institute Board of Trustees and Technical Advisory Committee and the sales organizations related to their respective mills, without whose help this program could not have been made, is also acknowledged with appreciation.

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Water-Resistant, Water Vapor Permeable Cotton Fabrics[1]

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Abstract

The water vapor transmission property of the cotton fiber is used to greatest advantage in plastic-coated, water-resistant fabrics when the coatings are relatively light, and are as much as possible located inside the fabric structure, with cotton exposed on each surface. "Hill and valley" structured fabrics such as narrow wale pique, poplins, drills and twills with prominent twill lines, and napped or pile fabrics, such as suedes or velvets with a substantial backing portion of the fabric, are advantageous. However, light coatings on 80×80 print cloth, well scraped into the surface, can also show favorable combinations of relatively low vapor resistance and relatively high hydrostatic resistance.

A plasticized resin latex with a substantial proportion of water-soluble thickener tends to give more porous films than the films produced by plastisols, but each approach can give a wide range of combinations of properties.

While the fabrics do show vapor and water resistances which compare favorably with commercial "breathable vinyl" upholstery fabrics, the appearance and feel are different. Many factors in addition to water vapor permeability and hydrostatic resistance need to be considered in commercial fabrics.

Objective and Background

The objective of this work has been to develop means of using cotton itself as a mechanism for obtaining vapor permeability in water-resistant fabrics. The growing use of impermeable vinyl films in upholstery has shown that there is a consumer demand for strong, durable fabric, which should be capable of being cleaned easily, as with a damp rag, but which would be more desirable if it had more vapor permeability than the usual type of vinyl upholstery. Likewise, the vinyl plastic raincoat is valued for compactness and economy, as well as waterproofness for moisture in the form of rain, but can seldom be worn in comfort for any extended period. There are many other fields in which a combination of a degree of vapor permeability with a high degree of water resistance would be desirable. Some of these are in footwear, gloves, special industrial or military protective clothing, and special wrapping materials as used in the meat packing industry [10]. There are also possible applications where relatively but not completely vapor-impermeable fabrics are desired. These are of course the same general type of material looked at from the other end of the range.

Personal experience indicates that there are certain limits in the comfort which can be expected even with highly permeable fabrics. There are conditions of environment and heat stress in which no type of clothing will permit sufficient evaporation to avoid heat burden and excessive sweating. Nevertheless, there is a much wider range of comfort for the water-repellent cotton raincoat than there is for the impermeable plastic-film raincoat, and the same applies to upholstery. This indicates that while there is an upper limit, set by the resistance of ordinary woven fabrics to passage of water vapor, there is a wide range in which improvement of comfort can be made.

Comparison of efforts to obtain water-resistant, vapor permeable materials by other means than by using the cotton fiber itself is instructive.

Table I shows the range of resistance both to liquid water and to passage of water vapor in water-resistant or vinyl-coated fabrics, and includes the range described in some patents for breathable compositions with rubber, neoprene, and similar elastomers. This table ranges from the ordinary water-repellent raincoat material to the continuous vinyl

[1] A report of work done under contract with the U.S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. This contract is being supervised by the Southern Utilization Research Branch of the Agricultural Research Service.

film. The problem of comfort in upholstery has been recognized by several of the leading manufacturers of vinyl upholstery materials. One company has approached the problem by printing small areas of vinyl film, to occupy roughly half the area [16]. This leaves the other half as a regular cotton fabric. Another company offers two styles of vinyl fabric with small isolated holes [6, 7]. These are definitely higher in hydrostatic resistance and vary over quite a range of vapor resistance. Although the vapor resistance is higher than that of water repellent fabric, it is of course low compared with the impermeable continuous films. Another type is microporous, with a sponge-like structure [14]. The pores here are much smaller, and many may not be continuous, so that both the hydrostatic and the vapor resistance are high compared with the regularly spaced, isolated holes. There are also patents on special methods of incorporating fillers, both water-absorptive, such as cellulose flock in the form of wood pulp [5], or even nonabsorptive fillers, such as calcium carbonate or other inorganic fillers, in appropriate amount [11, 15] to render the film partially water vapor permeable. Other patents attempt to take advantage of incompatibility or nonadhesion between certain coating materials and certain fibers, to provide a system of pores [2]. All of these approaches are different from the objective of the present work, which is to use cotton itself as the means of transmitting water vapor.

One reason for expecting cotton to be useful in transmitting water vapor is the general impression of relative comfort of cotton fabrics compared with tightly woven fabrics made from nonabsorptive fibers [4]. Work done in 1947 showed that all types of fiber, if woven in the ordinary range of weaving densities, were almost equally permeable to water vapor, but that if the weaving density was increased, or the fabrics were compacted by calendering, or if the fiber was extremely low in water absorption, such as vinyon or glass, at high weaving densities, a definite increase in resistance could be observed [9]. Goodings and co-workers in 1955 [17] showed that there is a further factor in the measurement of water vapor permeability of thin fabrics, namely a blocking effect which is additional to the effect of the thickness of the fabric. This does not disqualify the 1947 results, however, since these were based upon increments of thickness by adding layers, rather than upon single layers. Goodings and co-workers investigated the ordinary weaving density range and likewise found that there was no distinct difference between one fiber and another. This emphasizes the fact that the passageway through air, which is available in ordinary woven fabrics, is much lower in resistance than any passageway through fibers. Hence, in order to determine the role of an individual fiber or type of fiber in conducting water vapor, it is necessary to accurately account for or eliminate the parallel effect of air channels.

Another factor which we had to consider at the beginning of this project was the fact that the vapor permeability of cellulose and other water-absorptive materials is greatly affected by the amount of water absorbed. Thus, cellulose films in the form of plain (non-moisture-proof) cellophane have vapor perme-

TABLE I. Commercial or Patented Water-Resistant or Coated Fabrics

Type	Reference	Air permeability, $(ft.^3/ft.^2)/min.$	Hydrostatic resistance, cm. water	Vapor resistance, cm. air	Symbol in Figures
I. Fabric pores exposed					
1. Water repellent, W.R.	12	1–10	10–50	0.1–0.3	A
2. SRRL tight weaving, W.R.	3	0.2	98	0.2*	SR
3. Vinyl printed on 50% of base	1, 16	half base*	0 unless W.R.	twice base*	
II. Fabric pores covered					
1. Breathable vinyl, regularly spaced isolated embossed holes	1, 6	0.4	14	4.8	B
2. Breathable vinyl, scattered holes	1, 7	0.3	11	19	C
3. Breathable vinyl, microporous	1, 14	0.3	91	22	D
4. Neoprene with solid filler	11, 15	0.0*	44–300	0.3–5.1	
5. Rubber with cellulose flock	5	low	71–104	1.1–5.6*	
6. Continuous vinyl		0.0	200+	66–350	

* Indicates an estimate.

abilities or resistances on the same order as that of an ordinary fabric at the relatively moist testing range, between 65% relative humidity and saturation, but are some thirtyfold less permeable or more resistant when one side of the cellophane is exposed to a dry atmosphere over calcium chloride or some other similar desiccant. (In order to obtain high resistance at all levels of humidity, the moisture-proof grades of cellophane are produced by an additional coating, usually composed chiefly of nitrocellulose.)

The lines of action undertaken in this project were: first, to measure the diffusion of water vapor through cotton fibers themselves, and second, to arrange systems of coated or plastic-treated fabric in which the water vapor permeability of cotton itself could be utilized. The results on diffusion of water vapor through cotton itself, and comparisons with other fibers, are reported separately [8]. They show the water vapor transmission of cotton to be roughly twice that of rayon and manyfold greater than that of Dacron [2] or nylon.

The practical development work to utilize the water vapor transmission advantage of cotton was done, in the main, by attempting to arrange so that cotton fibers would be exposed on each side of the combined fabric. However, since the influence of moisture on the transmission of water vapor by cotton is so great, it seemed advantageous to do some experiments in which the film itself might be made more permeable, either by pores in the film, or by appropriate fillers in the film, and to explore using cotton flock as such a filler.

Results with Coated Fabrics

In considering the type of water barrier to combine with the fabric, one might think it possible to pick a water barrier material which would itself be relatively high in water vapor permeability. Such materials do exist, or at least have a reputation in the packaging field for high water vapor permeability. Examples are cellophane (unless made moisture-proof), polyvinyl alcohol, carboxymethyl cellulose, cellulose acetate, and ethyl cellulose. All of these materials make rather stiff hard films, and are hardly the type materials to use with a flexible material such as cloth. The general association of high water vapor permeability with high number of polar groups leads to a relative stiffness of structure and low extensibility, while flexibility and extensibility in the film are accompanied by nonpolar groups and by low affinity for and transmission for water vapor. Thus, the more flexible, extensible, long-range elastic types of films are represented by polyethylene, rubber and other elastomers, and plasticized vinyl chloride polymers and copolymers. Rubber materials have been the subject of numerous patents for methods of making them relatively water vapor permeable. These patents imply that the methods will also apply to vinyl films and to practically all coating materials, but the claims and examples of practice are usually limited to compositions involving rubber or the synthetic long-range elastomers made into solutions or "cements" [5, 11]. These are usually applied to fabrics by calendering procedures. We have limited ourselves to vinyl chloride latex and plastisol, which are accessible to laboratory handling and to the equipment of most cotton textile finishers, since special laminating calenders, plastic or rubber mills, solvent recovery systems, and precautions against explosion of solvent vapor are not required for latices or plastisols.

Our objective, to have cotton exposed on both sides of the coated fabric, is different from that of the usual coating technique. The usual coating technique desires to have as little of the coating lost in the interior of the fabric and as much carried as a surface layer as possible. Such surfaces have a characteristic vinyl or artificial leather appearance. In most of the fabrics produced in this work the threads and cloth structure are partly visible from both surfaces, a result obtained by using relatively fluid coating mixtures, and by scraping hard to remove excess, rather than by operating to deposit as thick a film as possible.

The main features of the two general procedures available for laboratory-scale operation in coating fabrics need be only briefly mentioned since detailed directions are available from the suppliers of plastisol or latex materials. In the plastisol technique, a relatively fluid mix of finely divided plastic particles in fluid plasticizer is prepared, spread on the fabric, and heated to a point at which the plastic dissolves in the plasticizer. This requires the fabric and coating to reach a temperature of 350° F., which is indicated by "smoke" or fumes which rise copiously from the material. To minimize high temperature breakdown of the vinyl polymer, a small amount (1 part in 100 parts resin) of any of a number of com-

[2] Du Pont polyester fiber.

mercial stabilizers offered for the purpose was included in the mix. On cooling, a continuous phase of plasticized vinyl plastic is obtained. The latex system also requires heating to fuse the individual latex particle, and to incorporate plasticizer if this is added as a separate emulsion. Latices combining resin and a nondiffusing plasticizer in preplasticized emulsion particles are available and were used in this work.

To use latex preparations by knife coating techniques, it is common to thicken the material by some small amount of high viscosity material. It seemed desirable to use for thickener a removable water-soluble material, such as methylcellulose or carboxymethyl cellulose. By using relatively low viscosity grades of these materials, it should be possible to increase the soluble content of the mixture and thus possibly obtain a microporous film, after removing the soluble material. Figure 1 shows some of the properties of coatings prepared in a series with increasing content of water-soluble material. The add-on was measured after washing to remove the solubles. The final add-on goes down as the high range of soluble material is reached. This indicates removal of film substances, both vinyl chloride and methylcellulose during the washing. In order to show the relationships with air flow through the fabric in the same way as with water and vapor, the reciprocal of air permeability, that is, the resistance, has been plotted. Thus all the properties shown: add-on, resistance to air flow, hydrostatic resistance, and resistance to passage of vapor, tend to increase together. The effort in this development is to minimize the increase of vapor resistance, and depending on the particular application, increase the hydrostatic resistance to the range required. The hydrostatic and vapor resistance of the material in Figure 1 are in a possibly useful range, up to somewhere near 30% soluble materials.

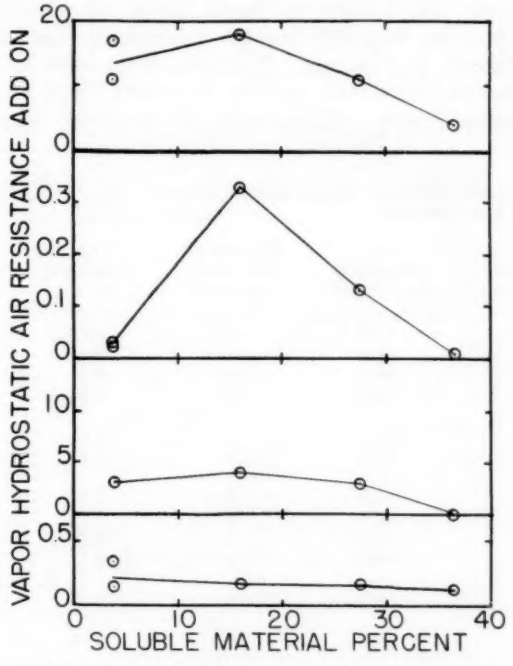

Fig. 1. Coated fabrics with increasing amounts of low viscosity carboxymethyl cellulose as soluble, removable thickener in the latex mixture. Coated with one pass, washed after curing. For other data see Table II.

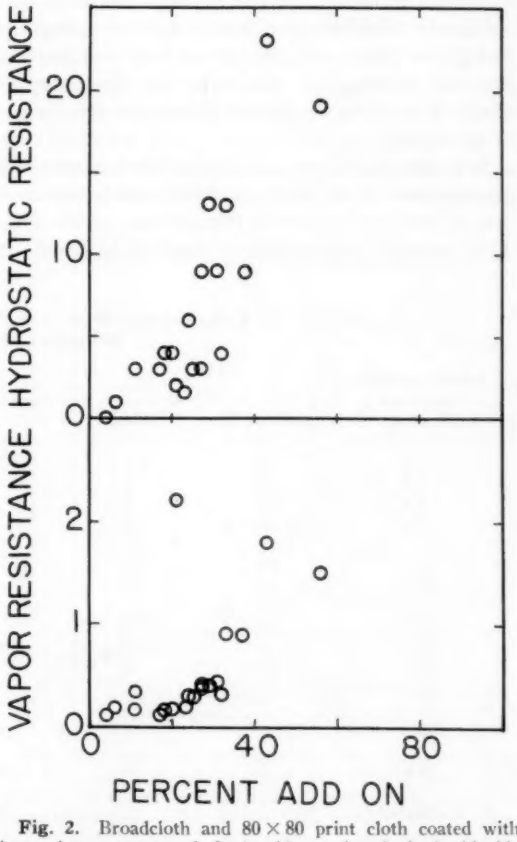

Fig. 2. Broadcloth and 80 × 80 print cloth coated with increasing amounts of final add-on of polyvinyl chloride latex.

While a comparison of results obtained with amount of water-soluble material in the coating is interesting from a special point of view, it is of more general interest to plot a wider range of preparations showing the properties of the resulting fabric against the final add-on itself. Figure 2 shows, in two panels, hydrostatic resistance, and vapor resistance, both increasing with increasing add-on. It should be noted, however, that the vapor resistance is in a relatively low range and the hydrostatic resistance in a useful range, for several of these preparations.

The variation in add-on can be obtained in several ways, while still fulfilling the objective of getting the barrier material within the fabric structure, in order to have cotton fiber exposed at the surface. Repeated passes of the coating knife, spreading the thickened composition each time, increase the add-on, as shown in Table II. One can also coat from both sides. In addition, after applying one coating and fixing the plastic in place by drying and heating, one can coat again. However, we have stopped short of building up plastic layers on the surface of the fabric.

It is also possible to use fillers with the latex-type preparation. Two types of fillers were examined, one, of obvious interest in this project, cotton flock. This proved a rather difficult material to handle in order to spread uniformly, but certain preparations were obtained which gave the results shown in Figure 3. Calcium carbonate was also examined, because it is a commonly used filler material, and because there is a patent of Habeck which cites its use in certain vapor permeable water-resistant rubber compositions [11, 15]. As with the plain latex preparations shown in Figure 2, both of the types with filler show an increase of resistance with increased add-on. Again it should be noted that some of these are in a useful range of vapor resistance. Although both of these types of preparations are relatively low in hydrostatic resistance, nevertheless, five or even fewer centimeters is sufficient for cleaning with a damp cloth and similar requirements.

For purposes of evaluating coated fabrics, it is useful to compare directly the vapor resistance on one axis with the hydrostatic resistance on another. Figure 4 shows such a comparison, for the range of the commercial fabrics shown in Table I. The letter A in the figure represents the range of woven water-repellent raincoat fabrics, which are low in vapor resistance and variable in hydrostatic resistance. SR indicates the special fabrics woven at the Southern Regional Research Laboratory, with extremely high pickage. B represents the more permeable of the two types of breathable vinyl with isolated holes. C represents the breathable vinyl

TABLE II. Latex Coatings on 80 × 80 Print Cloth, Carboxymethyl Cellulose Thickener (Hercules CMC-70 Low Viscosity)

Soluble material based on total solids, %	Add-on, %	Passes	Air permeability, $(ft.^3/ft.^2)/min.$	Air resistance, $min./(ft.^3/ft.^2)$	Hydrostatic resistance, cm. water	Vapor resistance, cm. air
3.8	17	1	38	0.03	3	0.14
3.8	11	1	53	0.02	3	0.34
3.8	24	2	16	0.06	6	0.30
3.8	25	2	17	0.06	3	0.29
16	18	1	3	0.33	4	0.17
16	31	2	0.9	1.11	9	0.46
27 6	11	1	7.7	0.13	3	0.16
27.6	20	2	19	0.05	4	0.17
27.6	27	3	2.2	0.45	3	0.38
27.6	32	4	3.5	0.29	4	0.32
36.4	4	1	63	0.02	0	0.12
36.4	6	2	63	0.02	1	0.19
Untreated			50.5		0	0.1

Reference to proprietary products does not imply endorsement of these over similar products produced by other companies.

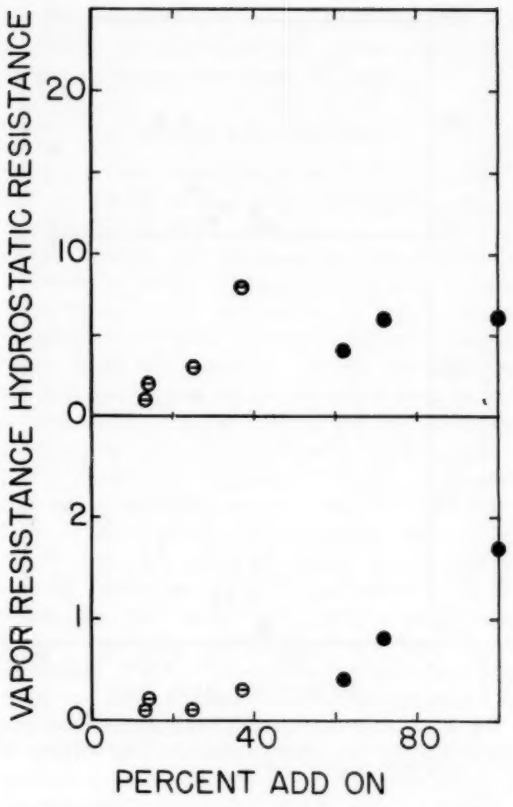

Fig. 3. Effect of cotton flock or calcium carbonate in latex coatings. Circles with horizontal lines, flock; solid circles, calcium carbonate.

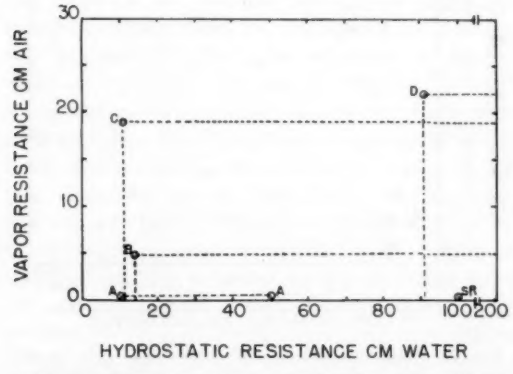

Fig. 4. Comparison of vapor and hydrostatic resistances of several commercial breathable vinyl upholstery fabrics. Letters designate materials of Table I.

with scattered holes and D, with its high hydrostatic resistance, represents the microporous type of vinyl coating. In the other graphs any fabric which lies beyond or to the right of the vertical dotted line or below the horizontal dotted line extending from a point representing one of the commercial fabrics will be superior to that commercial fabric in hydrostatic resistance if it lies to the right or in vapor resistance if it lies below. It should be emphasized that there is a wide range of combinations of vapor resistance and hydrostatic resistance which will be useful or needed for various purposes, but that for purposes of comfort, low vapor resistance, and for purposes of protection, high hydrostatic resistance are desirable. These same dotted lines are used on various other graphs, some of which are drawn to other scales, to facilitate comparison of the laboratory fabric preparations with the commercial range. Thus Figure 5 shows the latex-coated fabrics on a plot of vapor resistance versus hydrostatic resistance. The vapor-resistance graph goes only to 2.5 cm. instead of the 30 cm. shown in Figure 4, since the vapor resistance of all of the latex-treated fabrics was relatively low. However, note that many of them have useful hydrostatic resistances above 5 or even above 10 cm. of water. It should be noted that

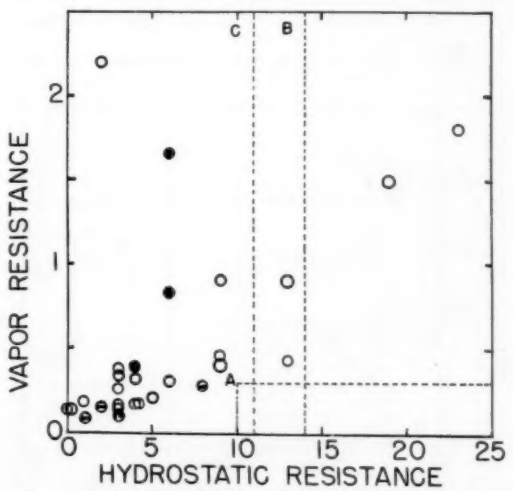

Fig. 5. Comparison of vapor and hydrostatic resistance for latex coatings on broadcloth and 80 × 80 print cloth. Dotted lines and letters indicate commercial breathable vinyl upholstery. Open circles indicate latex without filler; circles with horizontal lines indicate cotton flock as filler, and filled in circles indicate calcium carbonate as filler.

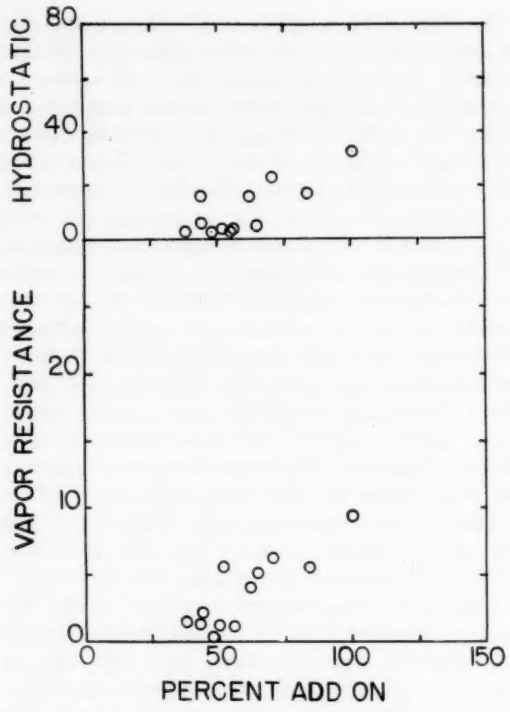

Fig. 6. Plastisol coatings on broadcloth and 80 × 80 print cloth, in relation to add-on.

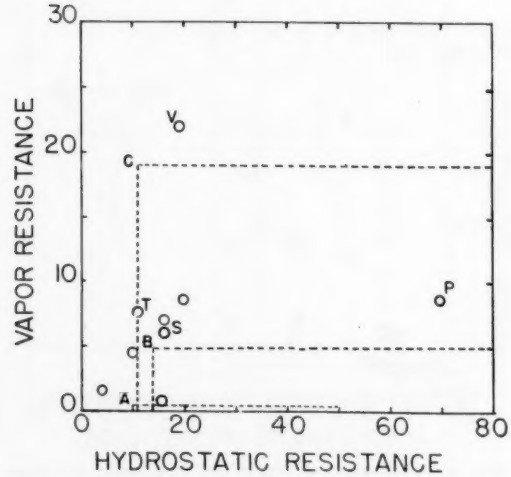

Fig. 7. Plastisol coatings on broadcloth and print cloth: comparison of vapor and hydrostatic resistances.

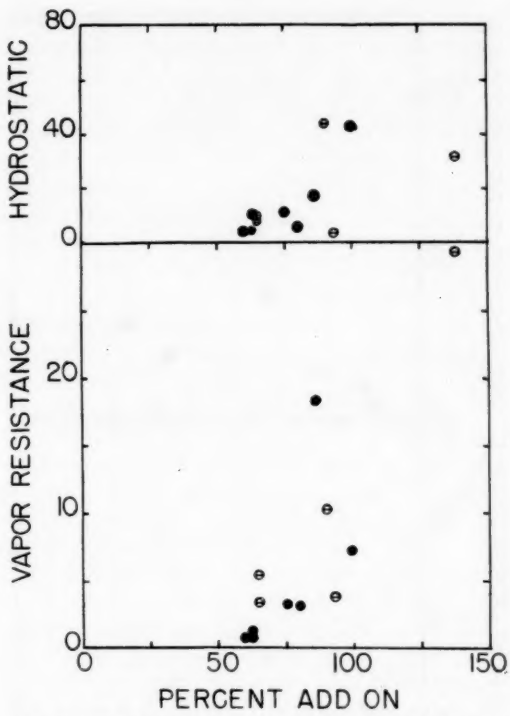

Fig. 8. Plastisol coatings with cotton flock (circles with horizontal lines) or calcium carbonate (filled circles) as filler, in relation to total add-on.

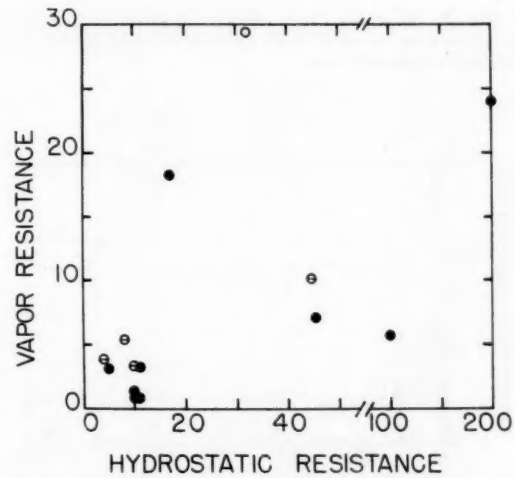

Fig. 9. Plastisol coatings with cotton flock (circles with horizontal lines) or calcium carbonate (filled circles) as filler: comparison of vapor and hydrostatic resistance. Two coatings at higher range of hydrostatic resistance than could be shown in Figure 8 have been added.

the fillers seemed to have had little effect, except possibly, in the case of the calcium carbonate in this system, to increase the vapor resistance.

Results with Plastisols

For the same general range of add-ons with plastisols there tends to be a somewhat higher range of vapor and hydrostatic resistance, as shown in Figure 6. It seems that the plastisols tend to produce a somewhat more continuous film than the latex preparations. This may reflect in part a microporosity of the latex system owing to imperfect fusion of the latex particles. It may also represent the influence of the soluble thickener, even in low concentration. Figure 7 shows the comparison of vapor against hydrostatic resistance for the plastisol-coated materials of Figure 6. These are plastisol coatings on either 80 square print cloth or a relatively tightly woven broadcloth shirting fabric. Figure 8 shows the effect of adding either flock or calcium carbonate as filler in the plastisol system. Again, the cotton flock systems were physically difficult to manipulate and to obtain satisfactory even spreading. Figure 9 shows that the range of hydrostatic and vapor resistances is somewhat higher than in the simple coating.

Another way of obtaining exposure of cotton fibers on both sides of the fabric is to take advantage of the weaving structure in fabrics which have pronounced hills and valleys in the structure. The broadcloth had a slight filling rib, and poplins with a more pronounced filling rib were also examined. Even more pronounced rib, this time in the lengthwise direction, was obtained with narrow wale pique. Results on these fabrics are shown in Figure 10. It may be noted that the vapor resistances in some of these are relatively low, and in Figure 11, which shows the vapor resistance against the hydrostatic resistance, it is seen that some very favorable results have been obtained with structured fabrics of this type. Another type of fabric which was examined was napped fabric. Flannel was tried but was not as successful as some of the other fabrics of firmer structure, such as velvet or suede. Although velvet and suede are much more expensive fabrics, it is possible to get a relatively impermeable, water resistant coat into the base fabric and leave a surface which has a nice hand and appearance. With flannel, the result is rather unsatisfactory; if one puts on enough plastisol, one gets a very leathery and

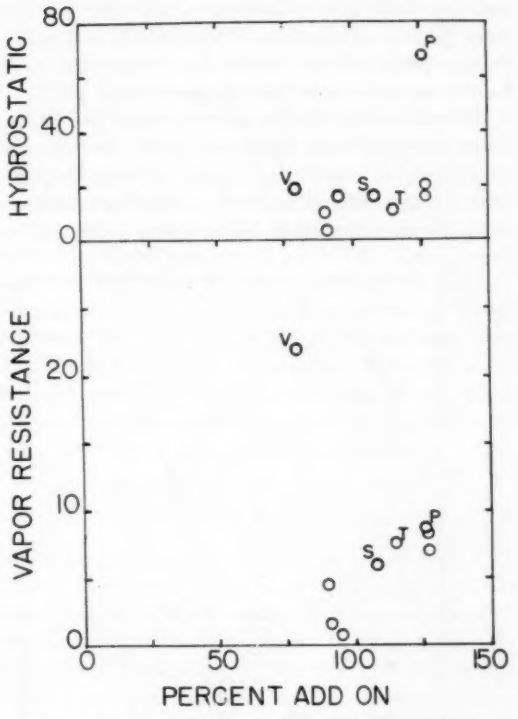

Fig. 10. Plastisol coatings on special fabrics. Open circles, narrow wale pique; circles with T, twill (drill); with P, poplin; V indicates velveteen, S indicates suede.

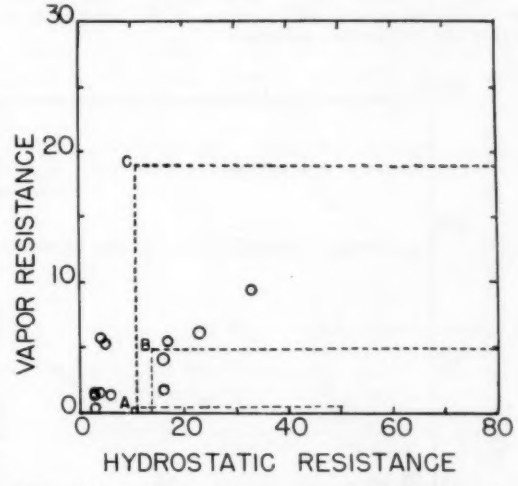

Fig. 11. Plastisol coatings on special fabrics, comparison of vapor and hydrostatic resistance. Symbols for fabrics as in Figure 10.

boardy effect, and if one does not put on very large add-on of plastisol, the fabric is still full of holes. Some of the results on velvet and suede fabrics are also shown in Figures 10 and 11.

In review, it is interesting to compare the general range obtained with latex treatments and plastisol treatments, as shown in Figure 12. As indicated from the figures and in the previous discussion, the latex treatments tend to lie at a lower level of resistance, both to vapor and to hydrostatic pressure, than the plastisol treatments. Many of the treatments shown in this figure are below 5 cm. hydrostatic resistance, which would have only a relatively limited range of usefulness. In order to show the higher range of hydrostatic resistance, a different scale has been used in Figure 13, in which the low hydrostatic resistances have been omitted. This figure shows that it is possible to prepare numerous types of combinations of cotton and plastic, which are relatively high in hydrostatic resistance, and are comparable to the perforated vinyl film in vapor permeability. At a relatively modest level of hydrostatic resistance, it is possible to have quite low vapor resistance. These fabrics, it may be added, have been rated at the point at which water began to ooze through them. There is only a slow rate of passage at much higher pressures, up to 200 cm.

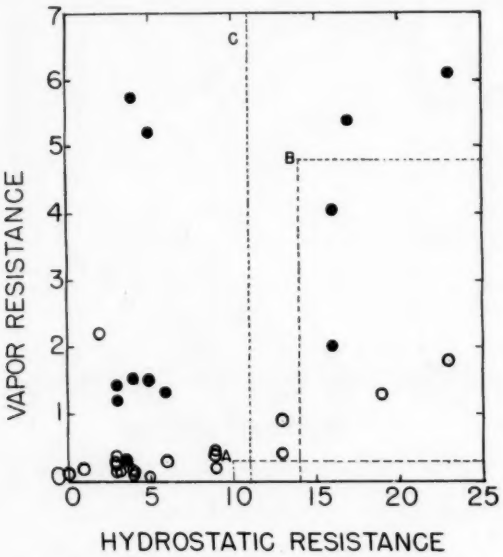

Fig. 12. Comparison of latex coatings (open circles) with plastisol coatings (filled circles) in the lower range of vapor and hydrostatic resistances.

Conclusion

While throughout this discussion our attention has been centered on the properties of water resistance and water vapor permeability, it must be kept in mind that for a useful, saleable fabric, there are other properties which require attention. The strength must be relatively unimpaired, the feel of the fabric and its flexibility must be satisfactory, and its appearance must be acceptable. These are matters which can be adjusted within rather wide ranges. The chief differences between the type of lightly coated or internally rather than surface-coated fabric produced in the present trials, and

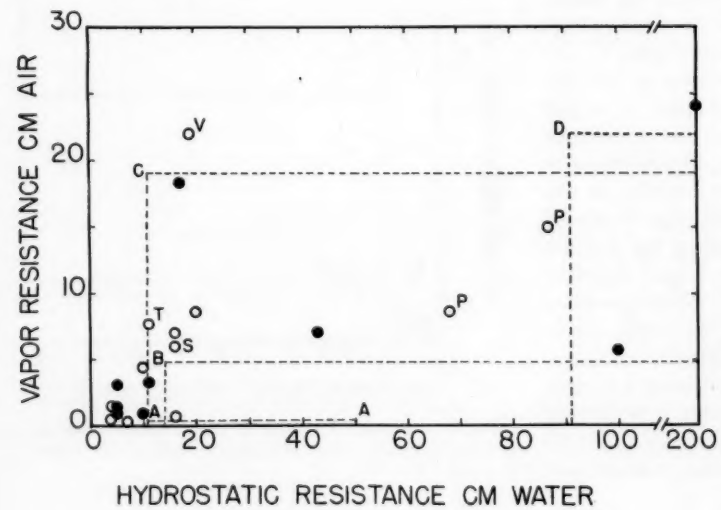

Fig. 13. Plastisol coatings on different fabrics, in higher range of resistances. None of the latex coatings, and none of the plastisol coatings on broadcloth or 80 × 80 print cloth of Figure 12 are shown here. Plastisol coatings with calcium carbonate as filler are represented by filled circles. Open circles without letters represent narrow wale pique. Open circles with letters represent: P, poplin; S, suede; T, twill (drill); V, velveteen.

the commercial fabrics are in appearance and feel, and possibly in durability. These are in part matters of taste and in part matters which will require extensive field testing should one wish to use these principles in practical fabric finishing and offer them to the public. It should be noted that in some current practice plastic or elastomeric coatings are applied to the back of woven decorative upholstery fabrics, and that the principles discussed here can also be used in this way, with advantages of appearance and feel or hand.

Appendix

Methods of Test

Add-on. By difference of conditioned weight, between original fabric and coated fabric. All latex-treated fabrics were washed. Plastisol-treated fabrics were not washed. Unit: per cent of original conditioned weight.

TABLE III. Latex Coatings on Broadcloth, with Methylcellulose as Thickener (Dow Methocel 4000 cps. Grade)

Soluble material based on total solids, %	Add-on, %	Passes	Air permeability, (ft.³/ft.²)/min.	Hydrostatic resistance, cm. water	Vapor resistance, cm. air
20	21	3	6.4	2	2.2
1.24	29	1	0.2	13	0.4
1.24	33	1	0	13	0.9
1.24	43	2	0	23	1.8
1.24	56	2	0	19	1.5
3.6	23	1	1.5	5	0.2
3.6	27	1	0	9	0.4
3.6	37	2	0	9	0.9
Untreated			143	0	0.13

Reference to proprietary products does not imply endorsement of these over similar products produced by other companies.

Air permeability. ASTM D737-46, using air pressure across fabric = 0.5 in. water. Unit: cubic feet of air per square foot of fabric per minute, or, in Figure 1, the reciprocal of this.

Hydrostatic resistance. ASTM D583-54, Method II. This is AATCC method 18-52. Unit: centimeters of water.

Vapor resistance. Single fabric layer held out of contact with a guard fabric, as described by Whelan, McHattie, Goodings, and Turl [17]. Unit: centimeters of equivalent diffusion resistance in still air. Calculation of experimental data by method of Fourt & Harris [9]. The resistance in centimeters of air can be calculated from the moisture vapor transmission, M, grams per square meter per 24 hr., if the relative humidity and temperature on the two sides of the specimen is known, by the relation:

$$R = K\ 1/M$$
$$K = D_a(C_1 - C_2)\ 10^4 \times 24 \times 60 \times 60$$

where D_a = diffusion constant of water vapor in air = 0.25 cm./sec. at 21° C., and C_1 and C_2 are the concentrations of water vapor, in grams/cm.³, corresponding to the two humidities. In all tests for this work the humidity inside the test cell was 100% (water) and outside 65% (ASTM standard atmosphere for textile testing) at 21° C. For these conditions, $K = 1390$. For transmission units of grams per square meter per hour, the corresponding constant is 58.

Materials *

Latex. Polyblend 550 × 20, B. F. Goodrich Chemical Co., vinyl chloride internally plasticized with nitrile rubber. Polyblend 552, same source,

* Reference to proprietary products does not imply endorsement of these over similar products produced by other companies.

TABLE IV. Latex Coatings with Filler, on 80 × 80 Print Cloth, 4000 cps. Methylcellulose as Thickener. Fabric Washed after Curing.

Filler	Amt. filler based on total solids, %	Amt. methocel based on total solids, %	Passes	Add-on, %	Air permeability, (ft.³/ft.³)/min.	Hydrostatic resistance, cm. water	Vapor resistance, cm. air
Cotton flock	18.8	2.0	1	13	19	1	0.1
"	"	"	2	14	10	2	0.2
"	25.6	20.6	1	25	4.8	3	0.1
"	"	"	2	37	4.1	8	0.3
Calcium carbonate	17	0	1	62	0.6	4	0.4
"	"	0	1	72	0.4	6	0.8
"	"	0	2	101	0.4	6	1.7

TABLE V. Plastisol Coatings. Stabilizer and Pigment Omitted from Coating Composition. Air Permeability below 0.2 (ft.³/ft.²)/min. unless Noted

Footnote	Base fabric	Add-on, %	Sides coated	No. of passes	No. of coatings	Coating composition, parts/100 parts polyvinyl chloride: DOP	Filler	Filler	Hydrostatic resistance, cm. water	Vapor resistance, cm. air
	Broadcloth	44	1	1	1	100	0		16	1.8
	"	43	1	1	1	100	0		6	1.3
	"	62	1	2	1	100	0		16	4.0
	"	71	1	2	1	100	0		23	6.1
a	80 × 80	48	1	1	1	100	0		3	0.3
a	"	84	1		2	100	0		17	5.4
a	"	101	1		2	100	0		33	9.7
b	"	high	1	3		50	0		high	71
c	"	38	1	1	1	50	0		3	1.4
	"	65	1	2	1	50	0		5	5.2
d	"	52	1	1	1	50	0		4	5.7
	"	56	1	2	1	50	0		4	1.5
	"	55	1	1	1	50	0		3	1.2
	Broadcloth	94	1	2	1	100	25	Cotton flock	4	3.9
	Broadcloth	65	1	1	1	100	25	Cotton flock	8	5.4
	"	65	1	1	1	100	25	Cotton flock	10	3.4
	"	138	1	2	1	100	25	Cotton flock	32	29.4
	"	90	1	2	1	100	25	Cotton flock	44	10.2
	80 × 80	63	1	1	1	100	50	Calcium carbonate	5	1.4
	"	60	1	1	1	100	50	("Atomite")	5	1.0
	"	100	1	2	1	100	50	" "	43	7.1
	"	103	1	2	1	100	50	" "	100+	5.8
	"	75	1	1	1	100	100	Calcium carbonate	11	3.3
	"	81	1	1	1	100	100	" (Surfex mm.)	5	3.1
	"	86	1	1	1	100	100	"	17	18.3
e, f	"	63	1	1	1	100	200	"	10	1.0
f	"	200	1	1	1	100	300	"	200+	24
f	"	268	1	1	1	100	300	"	200+	49
g	Pique, narrow wale	82	1	1	1	100	0		7	0.3
h	"	75	1	1	1	100	0		4	0.5
i	"	95	1	1	1	100	0		16*	0.7
	" B	91	2		2	75	0		10	4.4
	" B	127	2		3	75	0		16*	7.0
	" A	91	2		2	75	0		4	1.5
	" A	128	2		3	75	0		20	8.6
	Poplin	126	1	1	1	100	0		68	8.7
	"	160	2	1	3	75	0		87*	15
	Drill	115	2	1	3	75	0		11	7.7
	Velvet	79	1		3	75	0		19	22
	Suede	108	1		3	75	0		16*	6.0

a. Fabric precoated with 2% solution of methylcellulose 7000 cps. grade, spread on by knife coater. This reduced the tendency of the plastisol to penetrate the fabric.

b. Thinned with Varsol to spread, but rather thick. The fabric had the typical appearance of a continuous film coated fabric.

c. Thinned with Varsol until rather fluid, like 100:100 mix.

Table V footnotes continued on opposite page

TABLE VI. Properties of Fabrics before Coating

Fabric	Weight, oz./yd.²	Air permeability, (ft.³/ft.²)/min.
Broadcloth	3.6	143
80 × 80 print	3.5	50
Poplin	3.6	85
Drill	5.1	82
Narrow wale pique		
a	4.5	83
b	3.7	84
Flannel	4.4	103
Velveteen	7.7	41
Suede	7.6	24

same type. Resin for plastisols. Polyvinyl chloride: Geon 121, B. F. Goodrich Chemical Co. Plasticizer for plastisols: various commercial dioctyl phthalates.

Stabilizer for plastisols. Various commercial liquid stabilizers. Used at 1% on weight of polyvinyl chloride.

Pigment. 5% suspension of Benzidine yellow in dioctyl phthalate. Used at 5% of this mixture on weight of resin and calculated as part of plasticizer.

Formulations. Latex systems were made up by combining relatively concentrated solutions of the thickening agents, methyl cellulose or carboxymethyl cellulose with the liquid.

After drying, the latex-treated fabrics were heated to 300° F.

Plastisols were made by mixing varied proportions of resin and plasticizer, from 1:1 to 2:1, in various sets of trials. In the high resin mixtures, a small amount of volatile mineral spirits (Stoddard solvent), up to 5%, on weight of resin was needed to give spreading consistency. Good results were obtained between 100 parts and 75 parts of plasticizer to 100 parts of resin. General recommended practice [13] was followed. Coated fabrics were heated in a 350° F. oven until "smoke" was given off, to fuse the plastisol.

Numerical results. The data which are shown in the graphs are given numerically in Tables II through VI.

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d. Scraper blade $\frac{1}{16}$-in. radius instead of $\frac{1}{4}$-in.
e. Air permeability 0.6 (ft.³/ft.²)/min.
f. High flash naptha added to spread.
g. Pretreated, one side, with 2% solution of 7000 cps. methocel. Air permeability 1.3.
h. Pretreated, both sides. Air permeability 3.1.
i. Water wets through at 16 cm, but only oozes slowly to at least 200 cm.

* Indicates hydrostatic pressures of wetting through, with slow seeping to much higher pressures.

Stable Ultraviolet Light Absorbers

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Abstract

It has been found that many substituted benzophenones are very effective as absorbing agents for ultraviolet light. Unlike most organic compounds which have been used for this purpose, this new class of absorbers is quite resistant to degradation. The physical properties and uses of these ultraviolet absorbers are discussed in detail.

The ultraviolet component of solar radiation extends from 400 down to about 290 mμ. A major objective in the development of stable organic absorbers has been to achieve a maximum of ultraviolet absorbing power with a minimum of visible color.

A variety of interesting applications have been found for these absorbers. They may be used in protective coatings or filters to protect substrates from ultraviolet light. They are usually quite effective as stabilizers when incorporated in ultraviolet sensitive materials. There are many potential applications of ultraviolet absorbers in the textile industry. They could be incorporated in fabric coatings or in finishes applied to yarns or fabrics that are known to degrade in outdoor exposure because of ultraviolet light. They can improve markedly the light fastness of those dyes which are faded by ultraviolet light. Some of the problems involved in these applications are discussed.

Introduction

The ultraviolet portion of solar energy has been considered an important factor in the degradation of many materials exposed outdoors. Much effort has gone into improving the light stability of dyestuffs, textiles, paints, and plastics. Major emphasis has been directed toward better inherent light fastness of such materials, but the use of organic additives as light stabilizers has received considerable attention in recent years.

Perhaps one reason why light stabilizers have not become as common as antioxidants, or heat stabilizers, is that most of them were not inherently light stable. Poor stability of an ultraviolet absorber may not be a handicap for use in a suntan lotion but it rules out applications in protective coatings and plastics. Of all the organic compounds that have been studied for use as ultraviolet absorbers, it is believed that derivatives of 2-hydroxybenzophenone are the most stable and most efficient. Compounds of this type are now marketed by General Aniline & Film Corporation under the trade name "Uvinuls" and by American Cyanamid Company under the designation "UV Absorbers."

Ultraviolet in Solar Radiation

Ultraviolet radiation from the sun ranges from 280 up to 400 mμ, the lower limit of the visible region. Actually, radiation at 280 mμ reaches the earth surface only under ideal conditions, and from a practical standpoint, we need to consider only the region between 300 and 400 mμ. The solar energy in this near ultraviolet region comprises about 5% of the total radiation incident on the earth. Figure 1 illustrates a portion of the radiation emitted by the sun, a tungsten lamp, and a daylight fluorescent tube.

It may be noted in Figure 2 that radiations in the lower ultraviolet region, 200 to 300 mμ, have a germicidal effect. Fluorescent tubes used for sanitizing action emit radiations in this region which are

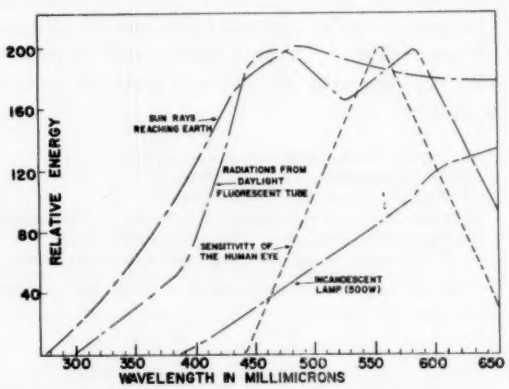

Fig. 1. Energy distribution of common light sources.

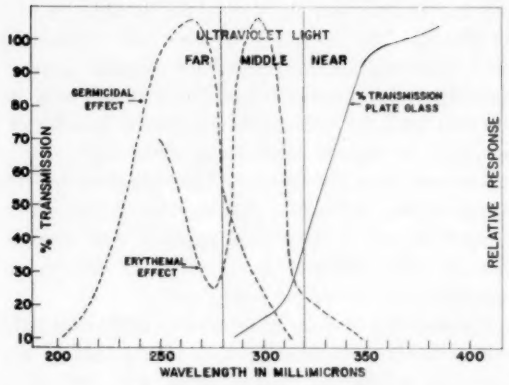

Fig. 2. Ultraviolet radiations.

lethal to many airborne bacteria. Radiations from 280 to 320 mμ have been shown to cause sunburn, while radiations between 320 and 350 mμ promote tanning.

In studying the action of sunlight on a dyestuff, a fiber, or a polymer, it is essential to establish first the relative importance of ultraviolet, visible, and infrared radiation. It is desirable also to know what region of the near ultraviolet is most critical.

Structural Requirements of an Ultraviolet Absorber

When an organic compound absorbs radiation, it is either raised to a higher energy level or dissociated. An "excited" molecule may dissipate the absorbed energy in a number of ways. It may dissociate, lose energy by collision, fluoresce, or react with other molecules at collision.

The photochemistry of polyatomic molecules is quite complex, and very little is known about photochemical mechanisms of organic compounds [13]. Certainly not much is known about the energy conversion processes in ultraviolet absorbers such as substituted benzophenones. Possibly the ultraviolet radiation raises the molecules to a higher electronic energy level, this energy is quickly converted internally to higher vibrational levels, and finally is dissipated as thermal energy by collisions.

An effective ultraviolet absorber would first of all absorb efficiently throughout the near ultraviolet region of the spectrum, particularly between 350 and 400 mμ. Second, the absorber must be stable itself to ultraviolet light. Third, the absorber must dissipate the absorbed energy in such a manner as to cause no degradation or color in the medium to be protected.

Without going into the history of ultraviolet absorbers or reviewing the many structures that have been studied, it can be stated that substituted benzophenones are the most effective compounds that have been found to date. VanAllan and Tinker [17] studied the UV absorption of a number of substituted benzophenones. As shown in Figure 3, they found pronounced differences in absorption between benzophenone, 4-hydroxybenzophenone and 2,4-dihydroxybenzophenone. The strong absorption in the near ultraviolet of 2,4-dihydroxybenzophenone is attributed to a conjugate chelation between the ortho-hydroxy and the carbonyl group. Since a hydroxy group ortho to a carbonyl is characteristic of stable ultraviolet absorbers, one could conclude that this structure is associated with the stability and internal energy conversions of these molecules.

The structures of several stable ultraviolet absorbers are shown in Figure 4. It is apparent that many structures are possible with different solubilities and compatibilities. The absorption curves for

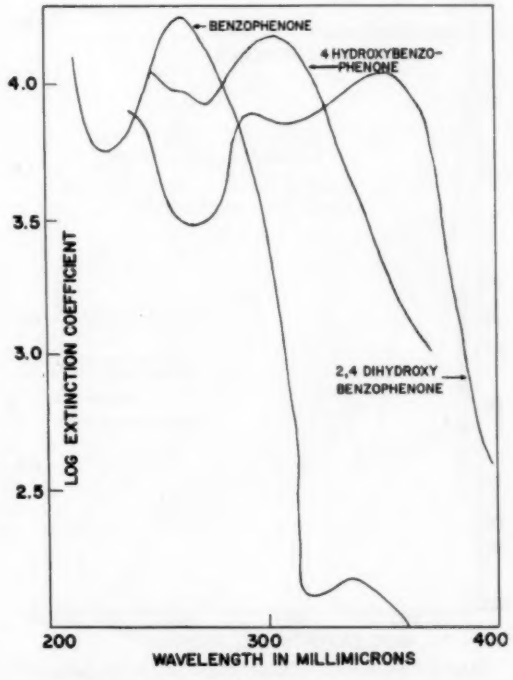

Fig. 3. Ultraviolet spectra of benzophenones.

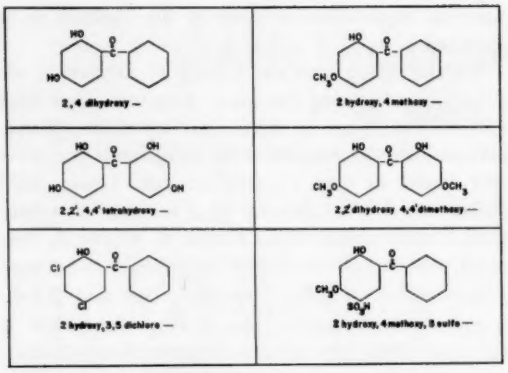
2,4 dihydroxy —
2 hydroxy, 4 methoxy —
2,2', 4,4' tetrahydroxy —
2,2' dihydroxy 4,4' dimethoxy —
2 hydroxy, 3,5 dichloro —
2 hydroxy, 4 methoxy, 5 sulfo —

Fig. 4. Stable ultraviolet absorbers of 2-hydroxybenzophenone type.

two compounds are shown in Figures 5 and 6, and the properties of these two absorbers have been described in a previous publication [9].

As can be seen from the absorption spectrum, 2,4-dihydroxybenzophenone has no absorption in the visible and is therefore colorless. The absorption curve of the other absorber, however, extends slightly into the visible, and the compound is light yellow. At 400 mμ, the boundary between the visible and the ultraviolet, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, is approximately ten times as powerful an absorber as 2-4-dihydroxybenzophenone and, therefore, will be equally effective at about 10% of the concentration of the latter. This suggests its use in applications where its yellow color is not objectionable and where the critical region is near 400 mμ. If a colorless material is essential, 2,4-dihydroxybenzophenone should be used.

The stability of these absorbers to ultraviolet light is illustrated by Figure 7 which shows the absorption of a polymethyl methacrylate film containing 2,4-dihydroxybenzophenone before and after 1000 hr. exposure in a Fadeometer. The importance of having the ortho-hydroxy group unsubstituted is shown in Figure 8. The compound 2-methoxy-4-hydroxybenzophenone is not considered a stable absorber. Similarly, Figures 9, 10, and 11 show that not all substituted benzophenones are stable.

Having shown that certain benzophenone derivatives absorb strongly in the near ultraviolet region

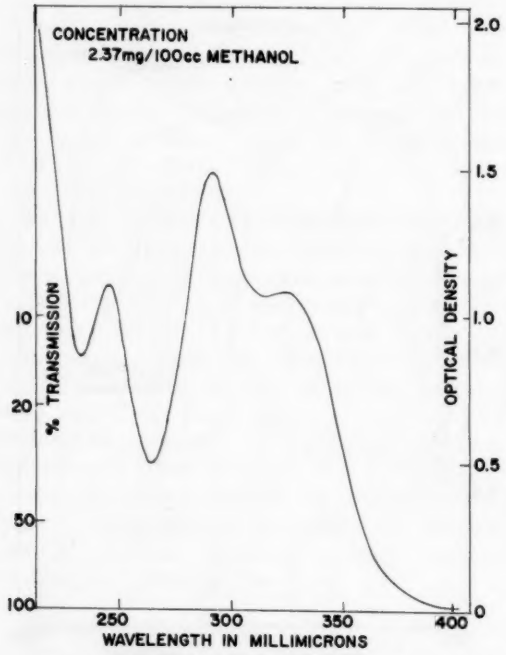

Fig. 5. Absorption characteristics of 2,4-dihydroxybenzophenone.

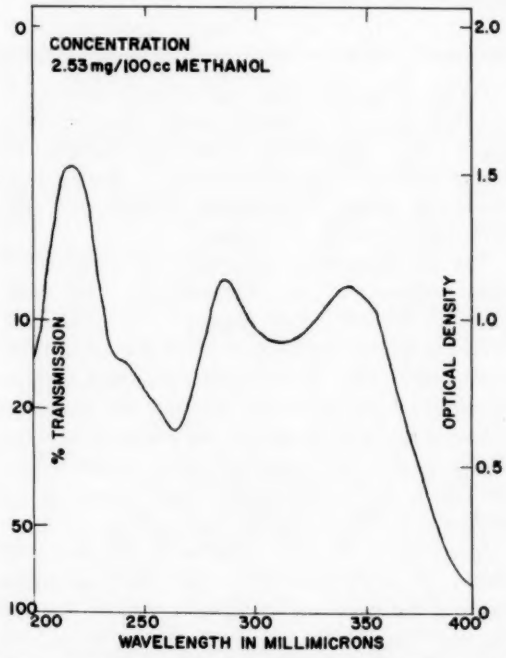

Fig. 6. Absorption characteristics of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone.

and that such compounds are not degraded by ultraviolet light, it must be established that the energy dissipated by these compounds is not deleterious. This can be done best by reviewing a number of applications for stable ultraviolet absorbers.

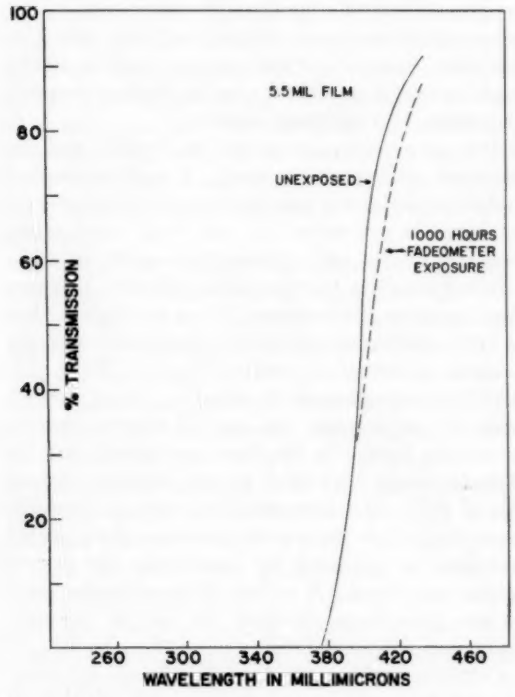

Fig. 7. Ultraviolet stability of 2,4-dihydroxybenzophenone in polymethylmethacrylate.

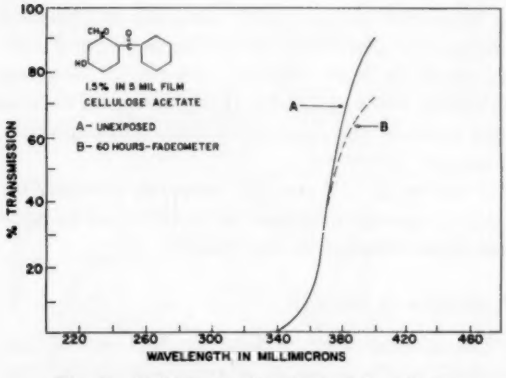

Fig. 8. Stability to ultraviolet of 2-methoxy, 4-hydroxybenzophenone.

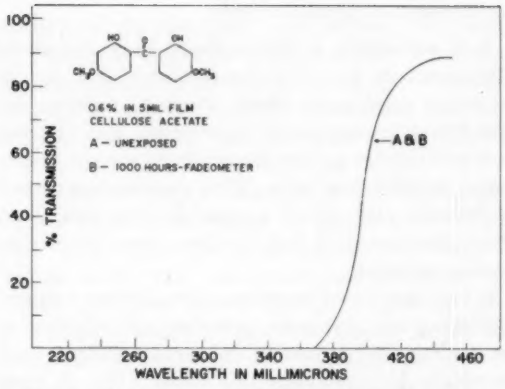

Fig. 9. Stability to ultraviolet of 2,2′-dihydroxy,4,4′-dimethoxybenzophenone.

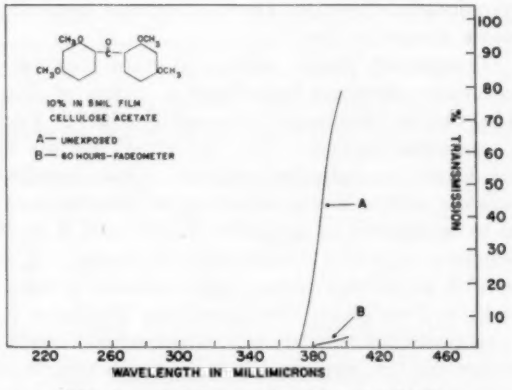

Fig. 10. Stability to ultraviolet of 2,2′,4,4′-tetramethoxybenzophenone.

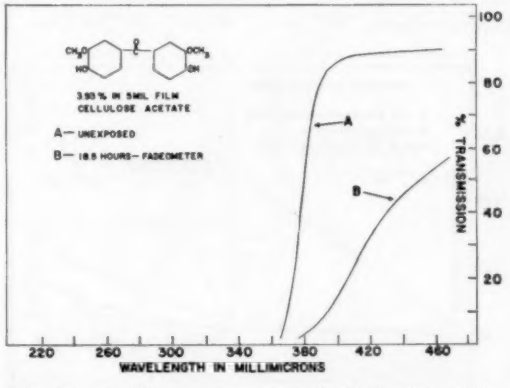

Fig. 11. Stability to ultraviolet of 3,3′-dimethoxy,4,4′-dihydroxybenzophenone.

Applications as Optical Filters

It is convenient to divide the uses of the stable UV absorbers into two classifications: (1) use in protective coatings or plastic sheets to serve as optical filters for protecting a substrate, and (2) use as a stabilizer in various materials to prevent degradation by ultraviolet light. This classification cannot be followed very strictly because in some cases both effects are operative and in other cases the mechanism is not clear.

It has been found that clear nitrocellulose lacquers containing an ultraviolet absorber are effective in preventing the darkening of certain natural and chemically bleached furniture woods [1]. A clear polymethylmethacrylate lacquer containing an absorber was found to give marked protection to polystyrene exposed outdoors [15]. Several other applications have been found for clear finishes containing stable ultraviolet absorbers.

Transparent plastic sheets and films containing ultraviolet absorbers have found a variety of uses. The Ozalid Division of General Aniline & Film Corporation markets a "UVHC Filter" for use in the Ozalid reproduction process. Clear, colorless cellulose acetate sheets containing an absorber seem to be as effective as the amber shades used in store windows to protect merchandise on display. It is possible to package various items sensitive to ultraviolet in clear plastic films containing absorbers.

In glazing materials, such as polymethyl methacrylate used in airplane windows or canopies, it is often possible to incorporate an absorber in the monomer before polymerization. Ultraviolet radiation, which becomes more intense at high altitude, can be screened out to prevent sunburn or other adverse effects.

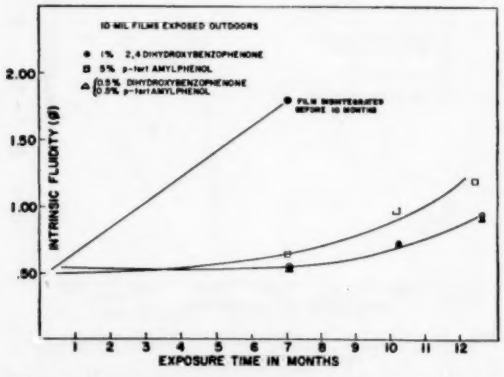

Fig. 12. Effect of stabilizers on the photo-oxidation of ethyl cellulose.

Application as Stabilizers

It has been known for many years that various polymeric materials are degraded by ultraviolet light [8]. Several companies have worked on this problem and many patents have been issued on formulations incorporating ultraviolet absorbers to improve weatherability. The problem is rather complex because plasticizers, antioxidants, and heat stabilizers are often involved. Furthermore, years of testing under practical conditions may be required to prove the merits of a stabilizer system.

Polyester resins are prone to discolor and deteriorate on outdoor exposure. A very pronounced stabilizing action has been found for 2-hydroxybenzophenones in polyesters [5], and most resin manufacturers market one or more light-stabilized types.

Vinyl chloride and vinylidine chloride polymers degrade under the influence of heat and light by loss of HCl, which catalyzes further breakdown, and subsequent oxidation of double bonds. When 2,4-dihydroxybenzophenone is added to a vinyl chloride resin, it can increase the rate of discoloration by ultraviolet light. It has been postulated that the thermal energy converted by the absorber initiates loss of HCl. If a heat stabilizer, such as a metallic soap is added to the system, however, the absorber functions as expected by stabilizing the system against ultraviolet. A variety of benzophenone compounds have been patented for use in chlorine-containing polymers [16].

Cellulosic resins are adversely affected by ultraviolet light and can be stabilized by addition of absorbers. Meyer and Gearhart showed that cellulose acetate butyrate could be stabilized against outdoor weathering by addition of phenyl salicylate as an ultraviolet absorber [12]. Presumably, the more efficient and more stable benzophenone-type absorbers would be more effective. Figure 12 shows the stabilizing action of 2,4-dihydroxybenzophenone in an ethyl cellulose film exposed outdoors in Wilmington, Delaware [3].

A variety of UV-sensitive materials in either organic or aqueous solutions can be protected by addition of an absorber to the solution.

Application in Textiles

The adverse effect of light on both natural and synthetic textile materials is quite well known. Although the subject is old, it is very complex and can be influenced by a variety of factors. Simple and economical methods of utilizing stable ultraviolet

absorbers to improve the light fastness and weatherability of textiles have not been established. To a considerable extent, then, this discussion must be limited to potential applications.

A major difficulty is determining what wave lengths of ultraviolet, visible, or infrared radiation are responsible for degradation. Other factors, such as mildew, presence of moisture, presence of oxygen, industrial fumes, sensitizing action of dyes or dulling pigments, can influence degradation during outdoor exposure. On the other hand, use of accelerated laboratory tests such as the Fadeometer may give unrealistic results since this device is known to have a higher percentage of ultraviolet energy than sunlight [4].

It might be thought that ultraviolet absorbers would find extensive use for upgrading light fastness of dyes. The possibility of stabilizing cheap fugitive dyes to compete with more expensive fast colors is intriguing. Several practical factors, however, render this application quite unlikely.

Consider first the problem of applying an absorber to a textile fiber or fabric. A water-soluble type would be ruled out for lack of wash fastness. Dipping the textile in a solvent solution of a water-insoluble absorber might leave a uniform surface deposit, but this would probably not be very fast to rubbing, washing, or drycleaning. The ortho-hydroxy group, which is considered essential to performance of the absorber, tends to make the compound soluble in alkaline solutions.

The best approach might be to incorporate the absorber in a resin latex and apply this to the textile item. Application of 5% latex solids as a uniform coating over a 20 μ diameter fiber would give film thickness of less than 0.25 μ, assuming equal densities of the fiber and latex polymer. However, the absorbing power of films decreases when they become thinner, as shown in Figure 13. Recalling that 25.4 μ make up one mil, it is obvious that only a small amount of ultraviolet radiation will be screened out by films of the order of 1 μ.

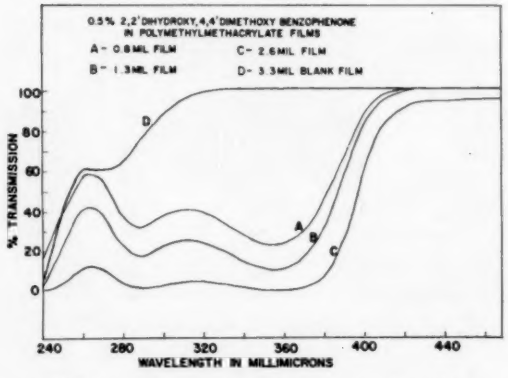
0.5% 2,2'DIHYDROXY,4,4'DIMETHOXY BENZOPHENONE IN POLYMETHYLMETHACRYLATE FILMS
A- 0.8 MIL FILM
B- 1.3 MIL FILM
C- 2.6 MIL FILM
D- 3.3 MIL BLANK FILM
% TRANSMISSION
WAVELENGTH IN MILLIMICRONS

Fig. 13. Effect of film thickness on absorption.

Another difficulty is encountered when the spectral regions which cause fading of dyestuffs are considered. A recent article by McLaren covers this subject in detail [11]. He found that ultraviolet and visible radiations caused fading of dyes up to a critical wave length. This critical wave length was in the red for the fugitive colors and in the blue for the light fast colors. This behavior is illustrated by Figure 14 taken from McLaren's paper which shows the contribution to fading of five spectral regions of daylight for the dyes used as British light fastness standards. Appel and Smith obtained similar results in a much earlier paper [2].

Since only 5% of solar radiation is in the ultraviolet, screening out this radiation would retard the fading of fugitive dyes only slightly. On the other

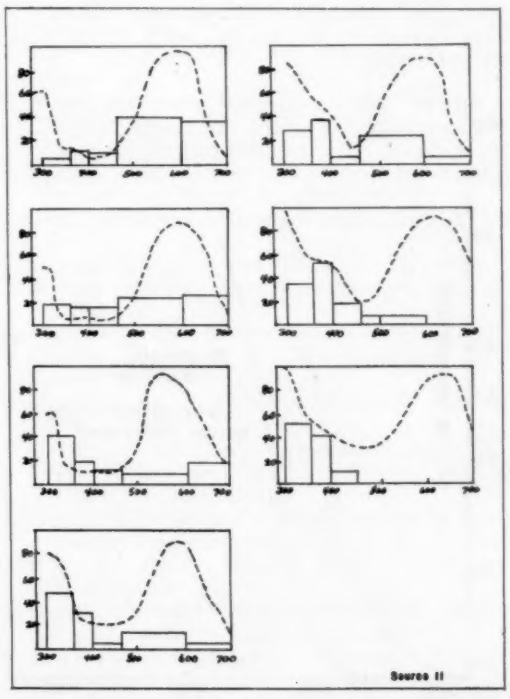

Fig. 14. Spectral regions causing fading. Reprinted by permission of the Journal of the Society of Dyers and Colourists, Figure 4 from McLaren, K., "The Spectral Regions of Daylight Which Cause Fading," **72**, 91 (March 1956).

hand, ultraviolet radiation is a major factor in the fading of the more light fast dyes, particularly yellows and oranges.

If the absorber were located in the fiber rather than in a thin surface film, it should be more efficient in protecting dyestuffs which are also within the fiber. Just how this might be accomplished in the case of natural fibers has not been determined.

Evidence has been obtained to indicate that some of the substituted benzophenones will penetrate into synthetic fibers much like acetate dyestuffs. The transmission curve of an aqueous dye bath containing an experimental absorber is shown in Figure 15. The shift in absorption after dyeing a nylon swatch for 45 min. at 95° C. in the bath indicates some exhaustion of the absorber onto nylon. It has been found also in certain cases that if an absorber is added to a regular dye bath, improved light fastness can be obtained. It is also known that an absorber can be incorporated into a spinning dope to improve the light fastness of certain pastel shades of spun-dyed fibers.

It appears that stable ultraviolet absorbers will find a number of special applications for improving the light fastness of dyed textiles. In each case it will be necessary to balance cost against performance.

There is also a possibility of using ultraviolet absorbers to enhance the weatherability of undyed textiles. The degradation of textile fibers has been studied extensively in sunlight as well as in artificial light. It is generally accepted that ultraviolet light plays an important part in fiber deterioration outdoors [6]. Dyes and pigments may retard the effect of light [7, 14] or act as sensitizers to increase the rate of degradation.

Several undyed fabrics were exposed in Charlotte, N. C., last summer for 30 and 60 days with and without a plastic cover containing an absorber. Exposures were made on a test rack facing South at a 45° angle, without glass, and for 24 hr. each day. The 6-mil plastic film effectively screened out all radiation below 400 mμ, as shown in Figure 16. The results of tensile strength measurements on these fabrics are shown in Table I.

With the reservation that other factors affect textiles on outdoor exposure, the data indicate that elimination of ultraviolet radiation greatly retards degradation. In the case of cotton and wool, there is a problem of applying absorbers, as pointed out earlier. It might be possible to incorporate absorbers during the manufacture of nylon and Dacron,[1] unless the high spinning temperatures involved cause too much degradation. Another possibility for these fibers would be to apply the absorbers from an aqueous solution by a dyeing process.

Jute is another fiber of considerable importance

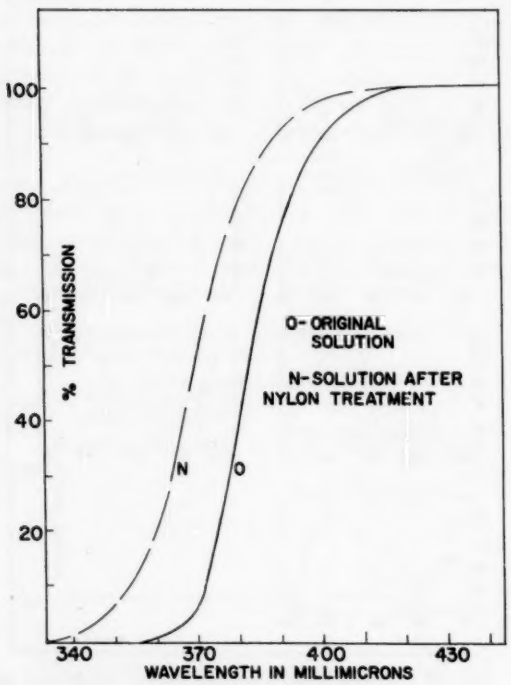

Fig. 15. Exhaustion of UV absorber on nylon.

TABLE I. Effect of Ultraviolet on Strength of Fabrics

Fabric	Exposure, days	Per cent loss of tensile: No filter	Per cent loss of tensile: With UV filter
Cotton	30	23	0
	60	28	23
Wool	30	34	12
	60	66	12
Nylon (delustered)	30	100	32
	60	100	37
Dacron (delustered)	30	44	5
	60	65	5

[1] Du Pont polyester fiber.

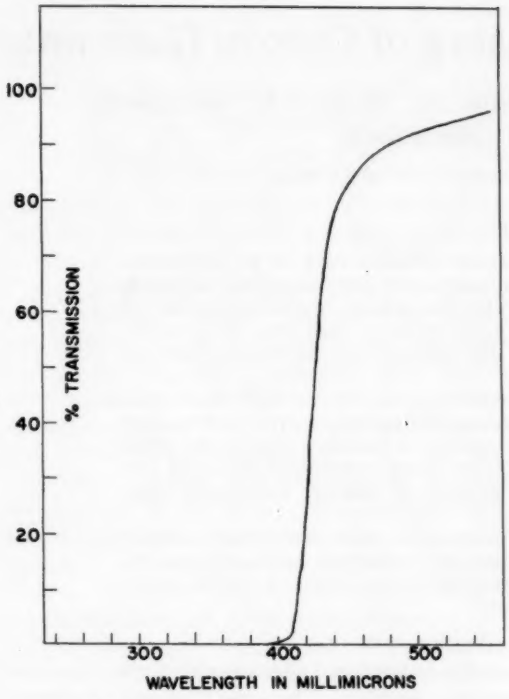

Fig. 16. Transmission of plastic film.

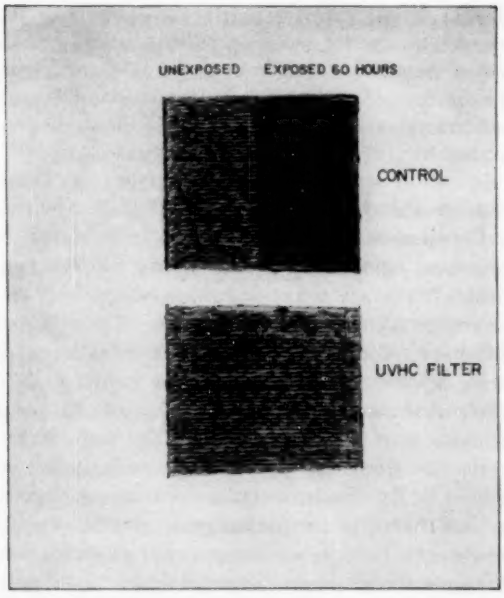

Fig. 17. Fadeometer exposure of jute.

that discolors and degrades in ultraviolet light [10]. Figure 17 shows the color change of jute yarn in a Fadeometer and the protective action of an ultraviolet filter.

Certainly, the surface has merely been scratched for textile applications of ultraviolet absorbers. One reason for this, of course, is the fact that the benzophenone-type absorbers have been commercially available for only a short time. However, since textiles are damaged by ultraviolet light, and since stable, efficient absorbers are now available, it seems inevitable that a number of textile applications for the absorbers will be found.

Acknowledgment

The authors wish to express their indebtedness to many colleagues in General Aniline & Film Corporation who have contributed to the discovery and development of stable ultraviolet absorbers.

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Studies on Permanent Creasing of Cotton Garments

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Abstract

The Southern Regional Research Laboratory has initiated work on the application of resin formulations to cotton garments for the express purpose of imparting permanent creases to them. In its full scope, the project has two phases: application to finished garments and application to yard goods, with resin curing in each case being accomplished on the finished garment. Advantages and disadvantages of the processes are described.

Methods of application, procedures, and results are given for application of a dimethylol cyclic ethylene urea (CEU) formulation to swatches of fabric and to garments. Description is given of the effect of a number of variables, such as the effect of storage on impregnated cloth, possibilities of stripping, precautions in drying and curing, durability to laundering, effect of sizing, effect of catalysts, and results using related resins in varying the formulation.

Ultimate objectives are given including cooperative work with other research agencies to utilize standard drycleaning equipment for commercial application, use on yard goods, and development of non-chlorine-retentive finishes suitable for white goods in imparting permanent creases to cotton garments.

PREVAILING fashion dictates that certain garments must be smartly and neatly creased and this crease must remain during the period the garment is being worn. The requirements of crease retention and wrinkle resistance properties of the garment are only moderately stringent in articles which are changed daily such as most shirts and blouses, but they are of extreme importance with such articles as men's trousers and ladies' skirts. In the field of men's dress slacks, for example, the natural comfort, durability, and launderability of cotton is sometimes rejected in favor of synthetic fibers because of the single factor of shape retention.

The present paper describes some studies on treatments for cotton designed to overcome this disadvantage and to allow cotton to compete on an equal basis with man-made fibers. The Southern Regional Research Laboratory recently has initiated work on the application of resin formulations to cotton garments for this purpose.

The rapid developments in the application of resins to cottons for the production of "minimum care," or "wash and wear" fabrics has been most impressive, and it is now an accepted fact that cottons can be produced which require little or no ironing after washing. There are, however, shortcomings to the present methods of treatment. In all cases the fabric is resin finished as piece goods and then made into garments. It is then difficult or impossible to sew flat seams or pockets. Furthermore cotton trousers or suits cannot be fabricated from the treated cotton because the formation of creases and cuffs is prevented. The object of the studies described here is to overcome this difficulty.

In its full scope, the project has two phases: application of resin formulations to finished garments and application to yard goods, with resin curing, in each case, being accomplished on the finished garment. There are a number of advantages and disadvantages to both of these processes. The principal advantage, of course, is that if the resin is cured in the finished garment, creases may be put exactly where desirable, seams and pockets are flat, and wrinkles may be eliminated from the body of the fabric. It would be better if the resin could be applied to flat goods, manufactured into garments, perhaps altered to suit the customer, and then cured. However, to produce satisfactory yard goods for this purpose a formulation is required which has almost indefinite shelf life after drying the fabric. There is

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

need for research to produce a catalyst, for existing resins or for a new resin, which would be sharply heat-sensitive. This catalyst should be completely stable up to an activation temperature low enough for applicability on standard garment pressing equipment, yet high enough to permit shelf storage of the fabric in the dried but uncured state. To date, no such product has appeared on the market. All catalysts in use at the present time cause some curing to take place over short or long periods of time even at room temperature. This precuring is detrimental to any subsequent curing operation. Any wrinkles present when this precuring takes place will remain through the final step. Moreover, sharp creasing may become impossible if storage is too prolonged. At the present time, it would appear that the process must be limited to garments.

In future research it is contemplated that work will be done on the other phases outlined above. Furthermore, it is hoped that in cooperative contract research commercially feasible methods of resin application and curing may be developed, perhaps by the use of commercial drycleaning equipment.

There is a rather large loss of strength and abrasion resistance in this type of resin treatment of fabrics. However, it appears that this loss of durability is offset by the appearance and convenience of use of the treated fabric.

The principal disadvantage encountered in treating garments lies in the methods of application. Centrifugation instead of the use of squeeze rolls must be employed to remove excess treating liquors. This raises the question of thorough and uniform distribution of resin. Second, a satisfactory, commercially feasible method of curing must be developed. A number of subsidiary difficulties must be overcome, such as the effect of the presence of sizing on the treatment, the possibility of correcting errors in application, and so forth. However, at present all of these problems lend themselves to easier solution than those which arise in the treatment of piece goods. The work described here, therefore, is concerned with the second phase mentioned above, namely, application of resin formulations to garments with subsequent curing.

Evidence from the litertaure, as well as the opinion of industrial representatives, indicated that the use of thermoplastic resins, in conjunction with the conventional thermosetting resins, for crease resistance, gave added improvements in physical properties of the fabrics [3, 5, 8]. Further, recent research on resin technology has demonstrated the superiority of the reactant-type resins, such as dimethylol cyclic ethylene urea (CEU) for wrinkle recovery [4, 9]. Although the work outlined in the present paper is confined to the use of CEU, other types of resins will be given consideration in future work. The finish obtained with CEU is very soft. In order to obtain a crisper finish, either a formulation embodying other resins now available or new resins as they are developed will have to be investigated. Possibly the incorporation of a small amount of another resin into the formulation described herein may provide the answer to the problem. Moreover, other resins may be found which do not cause as great a loss in strength and abrasion. It is also quite possible that the mechanism of catalysis for some other resin may be suitable for the thermal-sensitive catalysis required.

Materials and Methods

Resin Formulation

For the work described here, the reactive resin used has been mainly Rhonite R-1,[2] but other CEU resins such as Dan River DR-13, Resloom E-50, and Zeset S have been used with equally good results. An acrylate thermoplast, Rhoplex S-1, was used. Except where otherwise stated, the resin formulation used was that recommended by an industrial representative [7] and consisted of 14 g. Rhonite R-1 (50% solids), 5 g. Rhoplex S-1 (35% solids), 1.5 g. Catalyst H-7 (35% solids) (a metal salt catalyst), 2 g. Decetex 104 silicone emulsion (40% solids), with 0.4 g. Catalyst XEY-21 (catalyst for Decetex 104), 0.1 g. Triton X-155 (softening agent), and 77.5 g. water.

This emulsion was used within a few hours after its preparation in all work reported herein. However, it was found to be stable and satisfactory for use, with a slight additional stiffness of fabric, even after more than 1-month storage, despite the fact that its catalyst had been added. This may seem to be a contradiction when it is considered that dried fabric begins curing immediately. However, the curing operation is primarily one of cross-linking of the cellulose rather than a polymerization of the CEU with itself.

[2] The mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

Application of Treatment

For convenience in assembling data, garments were not used in the preliminary experiments; rather, a 4-oz. desized and bleached 80 × 80 cotton print cloth was used. To ensure uniformity of application, the cloth was padded instead of being centrifuged. The standard padding procedure was two dips and two nips with the final wet add-on being approximately 70%. After padding, samples were either oven-dried before curing by ironing, or were dried and cured in one operation by ironing from the wet state. Textile tests were performed under controlled conditioning of 70° F. and 65% relative humidity, employing standard methods for the following tests: wrinkle recovery angle by the Monsanto method [2], tearing strength by the Elmendorf method [2], flex abrasion by the Stoll method [2], strip breaking strength [2], and chlorine damage [1]. For convenience, the same bar was used on all fabrics to determine flex abrasion. Considerable reliance was placed on personal judgment of appearance of creases and smoothness of fabric after laundering. Laundering was generally carried out in a small apartment-size washing machine for 20 min. at 50°–60° C., at constant load, using a commercial home detergent. Nitrogen determinations were made by the standard Kjeldahl method.

Experimental and Discussion

Drying and Curing

Swatches of cloth 12 × 12 in. padded with the standard emulsion were dried on pin frames, without tension, in a forced draft oven at 60° C. (140° F.) for 7 min. before curing or were dried and cured directly from the pad in one operation. Curing was accomplished by use of an ordinary standard electric hand iron at about 180° C. (356° F.). Best results were obtained when the cloth was dried and cured by ironing immediately after padding. Poorest results were obtained when the cloth was dried at elevated temperatures before curing. In the treatment of garments, the most convenient method would be one in which the garment could be dried and then cured by ironing later, with considerable latitude in the storage time. It was found that drying temperature and length of storage in the dry state had a very great effect upon the results. In this work, duplicate samples of cloth were stored at temperatures varying from 30° C. (86° F.) to 80° C. (176° F.) for appropriate periods of time. One of the duplicate samples was then laundered and resin retention was determined by weighing and checked by nitrogen analysis. Data on these samples are shown in Figure 1.

The other duplicate samples were further cured by ironing for subjective evaluation of appearance. In these samples, creases were ironed warpwise, fillingwise and diagonally across one corner.

In this work and under the conditions outlined, the highest retention of resin obtained, after laundering, was approximately 80% of theory, as calculated from the resin content of the emulsion and the wet pickup on the fabric. From Figure 1, it may be seen that 80° C. is too high a drying temperature because even at 8 min. drying time, 68% of the possible resin is bound in the fabric. Although drying times of less than 8 min. are not given, shorter times were tried, but the fabric did not feel dry to the touch and these results are not included. At the higher temperatures (60° and 80° C.), none of the dried samples shown in the figure could be satisfactorily

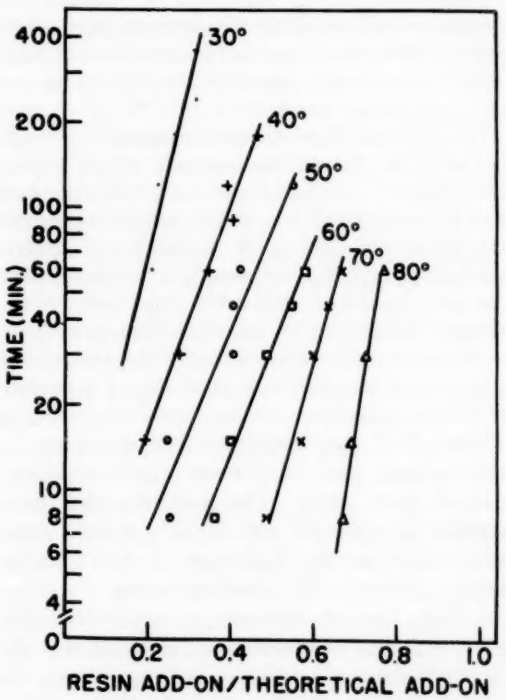

Fig. 1. Change in resin add-on with time and temperature of storage.

creased. While samples dried for a short time at the lower temperature could be acceptably creased, even 3 hr. at 30° C. was long enough to prevent satisfactory creasing or curing. When samples are stored dry at 30° C. (summer temperatures) for 60 hr. after padding, it is virtually impossible to iron in a crease which will survive one laundering cycle.

From the above results, it was concluded that in the treatment of garments, the curing operation would have to be integrated closely with the drying procedure. Although it might not be practical in commercial work, for optimum results the drying and curing operations should take place in one operation. By ironing while still wet, undesirable wrinkles acquired in padding may be removed before curing takes place. This is of even more importance when centrifugation is used instead of padding. Furthermore, the swollen cotton fibers are probably in an optimum condition for cross-linking reactions to take place and presumably this is a factor in the better crease obtained. One disadvantage in curing in this manner is the fact that formaldehyde is released during the cure, something which did not occur when the dry cloth was cured. It was therefore necessary to provide adequate ventilation during the ironing.

Variation in Commercial Resins

CEU sold under various trade names was obtained and used in the resin formulation. One set of samples was oven-dried at 60° C. for 7 min. before ironing; the second set was dried and cured in one operation. From the data in Table I, it may be seen that the four resins were essentially equal. The samples which were dried and cured in one operation were slightly better than those which were dried first, according to the data given. The appearance of the former, however, was greatly superior to the latter.

Launderability

The creases put in by the ironing of the wet samples display truly remarkable resistance toward simulated home laundering. At a temperature of 50°–60° C. (122–140° F.) and using a commercial detergent, treated samples of the print cloth withstood twelve 20-min. laundering cycles without any change in the appearance of the creases. In all cases the samples were laundered in the washing machine, rinsed, centrifuged, and ironed dry after each cycle. The wet cloth pieces were ironed flat attempting to iron out the creases rather than trying to retain them. However, in spite of this the creases remained sharp throughout the 12 laundry cycles and there was no great difference between the warpwise, fillingwise and diagonal creases. Data on this series are given in Table II.

Damage to resin-treated garments by bleaching during laundering is often cited due to the reaction of chlorine with the nitrogenous resins. However, Howard [6] has pointed out the superiority of CEU

TABLE I. Treatment of 80 × 80 Cotton Print Cloth with CEU Resin Formulations

CEU Resin*	Cure†	Wrinkle recovery angle, deg.		Flex abrasion,‡ cycles		Tearing strength, lb.		Breaking strength, lb.		% Breaking strength remaining after	
		W	F	W	F	W	F	W	F	Chlorine wash	Chlorine wash-scorch
No. 1	O	162	157	100	83	1.3	0.7	28.2	20.4	98	94
No. 1	I	150	152	210	200	1.3	0.8	29.3	22.6	107	98
No. 2	O	161	158	79	50	1.2	0.8	27.0	20.2	104	98
No. 2	I	157	153	190	91	1.4	0.8	33.3	20.8	95	89
No. 3	O	160	156	90	73	1.2	0.9	29.0	21.0	98	96
No. 3	I	155	152	130	160	1.3	0.8	27.6	22.1	108	106
No. 4	O	156	150	210	150	1.3	0.9	29.3	23.7	101	97
No. 4	I	152	146	160	130	1.4	0.8	31.7	23.6	96	95

* Commercial CEU resins from four companies were used.

† O = Oven dried under forced draft at 60° C. for 7 min. before curing by ironing. I = Dried and cured in one operation by ironing.

‡ Bar load 4 lb., head load 1 lb.

TABLE II. Launderability of Creased Fabrics*

Number of cycles†	Nitrogen content, %	Tearing strength (warp), lb.	Wrinkle recovery angle (warp), deg.	Appearance of creases
0	0.98	1.3	152	Excellent
1	0.97	1.3	147	Excellent
2	0.97	1.3	144	Excellent
6	1.00	1.3	145	Excellent
12	0.90	1.3	139	Excellent

* Samples treated with standard CEU resin formulation, dried and cured in one operation with hand iron. Resin content of sample was 4.8%.

† Samples laundered at 60° C. for 20 min. at constant load using a commercial home detergent.

resins over urea- and melamine-formaldehyde resins in this respect. This work is corroborated and the small amount of damage due to retained chlorine, after one treatment with sodium hypochlorite, as determined by the "scorch test" [1], is shown in the data of Table I.

Effect of Add-On

The effect of add-on of the resin formulation on the textile properties and appearance of the treated fabric was investigated. The add-on was controlled by varying the solids content of the treating solution which was padded onto 80 × 80 print cloth to about 70% wet add-on and cured from the wet state with a hand iron. The cloth was then given a mild laundering to remove uncured solids. The results are given in Table III and show the variation in appearance, wrinkle recovery angle, tearing strength, and resistance to flex abrasion.

Above 4% add-on is needed for good wash and wear appearance of the creases. Poor appearance resulted below about 2% add-on. Samples with 2 to 4% add-on were rated as good, but the creases were not as sharply defined as when 4% was reached. The wrinkle recovery angle of all samples except those with the lowest add-on was good, ranging up to 161°.

TABLE III. Effect of Resin Add-On on Appearance and Textile Properties of Treated 80 × 80 Cotton Print Cloth*

Add-on, %	Appearance of creases	Wrinkle recovery angle (warp), deg.	Tearing strength (warp), lb.	Flex abrasion† (warp), cycles
0 (untreated)	—	85	2.5	500
1.7	Poor	116	1.8	420
2.8	Good	137	1.6	310
3.4	Good	133	1.6	240
3.8	Good	139	1.6	200
4.9	Excellent	149	1.5	180
5.6	Excellent	154	1.3	170
7.4	Excellent	161	1.4	130

* The data given were obtained using Rhonite R-1 in the formulation. Use of Dan River resin DR-13 gave almost identical results.

† Bar load 4 lb., head load 1 lb.

Effect of Sizing

It is probable that garments containing various amounts of starch sizing would be submitted for resin treatment if the process were to be carried out on a commercial scale. Such a process would be far more useful if desizing were unnecessary. Therefore, the effect of sizing was investigated by comparing treatment of a warp-sized and a desized sample of 80 × 80 cotton print cloth. Results obtained with both samples were excellent and the physical data are in good agreement, as may be seen by a comparison of the data of Table IV with that of Table II previously mentioned. It was thought that the CEU might react with the starch size instead of the cellulose and come off in laundering. However, there was little loss of weight on laundering. The crease was resistant toward laundering and treatment with a desizing enzyme. Both the crease angle and appearance were unchanged. If reaction does occur with the size, it apparently does not harm the finished cloth. Perhaps the starch is cross-linked to the cellulose.

TABLE IV. Launderability of Creased, Sized Fabric*

Number of cycles†	Nitrogen content, %	Tearing strength (warp), lb.	Abrasion resistance‡ (warp), cycles	Wrinkle recovery angle (warp), deg.	Appearance of creases
0	1.09	1.5	270	155	Excellent
2	1.06	1.6	270	157	Excellent
3	0.94	1.5	230	147	Excellent
6	1.00	1.4	140	156	Excellent
12	0.99	1.4	150	154	Excellent

* Samples treated with standard CEU resin formulation, dried and cured in one operation with hand iron. Resin content of sample was 4.4%.

† Samples laundered at 60° C. for 20 min. at constant load using a commercial home detergent.

‡ Bar load 4 lb., head load 1 lb.

Stripping of Wash and Wear Finishes from Cotton

It is contemplated that custom application of resins to give permanent creases, for example, to cotton trousers, might well be carried out in a drycleaning establishment. An important phase of the development of a satisfactory process would be the ability to remove unsuccessful treatments. An error in pressing cannot be rectified by further pressing and only a few errors would be required to make the treatment unprofitable to the drycleaner. Thus the successful removal of the treatment and re-application could mean the difference between commercial feasibility and failure of the process.

The preliminary results reported here indicate that a treatment analogous to the "spotting" of stains by drycleaners might be successful. Further work and investigation of other methods will be necessary; however, the following procedure gave good results.

Methylol resins may be stripped from cotton fabrics by mild acid hydrolysis, the fabric returning to its original properties with practically no loss of strength, a fact which has been mentioned many times in the literature with regard to the removal of melamine-formaldehyde resins. CEU is much more easily hydrolyzed and removed than the relatively stable melamine-formaldehyde resins.

The resin formulation on the cured cloth contains the CEU resin, a polyacrylate thermoplastic resin, and a silicone polymer. The CEU resin may be stripped from the cloth by treatment with 1.5% phosphoric acid—5% urea solution at 80° C. for 30 min. Part of the original formulation, however, remains on the cloth. Presumably this is the thermoplast and the silicone. The polyacrylate may be removed with benzene, acetone, or methyl ethyl ketone. A solvent or other means of removing the silicone has not yet been found. Since, however, the silicone is only a small part of the formulation, its removal is not necessary.

The major portion of the resin, the CEU, is removed by acid hydrolysis. This has been verified by complete loss of nitrogen content, loss of finishing add-on, and restoration of the original properties of the cotton fabric. Solvent extraction, for example, with acetone, further reduces the add-on through removal of the polyacrylate thermoplast.

In Figure 2 are shown, as percentages of the original fabric property, the effect of resin treatment, changes by stripping of the resin by hydrolysis, further change by solvent extraction and restoration of properties by re-treatment. It may be observed from the figure that the resin treatment greatly increases the wrinkle recovery and causes a considerable lowering of tearing strength and abrasion resistance. Acid hydrolysis brings these values back approximately to those of the original fabric. Solvent extraction changes these properties very little.

Re-treatment of either the acid-hydrolyzed or the hydrolyzed and solvent-extracted fabric with the original formulation restores the properties to essentially the same points as those of a fabric treated directly with the formulation.

Samples treated with the resin formulation were acid hydrolyzed and then re-treated with CEU. Significantly, the results were excellent with properties equal to those of cloth treated with the original formulation. In this case, the solution of the CEU, with catalyst, was dried and cured by hand ironing. Apparently, the properties due to the thermoplast remained from the first treatment. This is further evidence of the interdependence of the components of this formulation since CEU applied to fabric, with

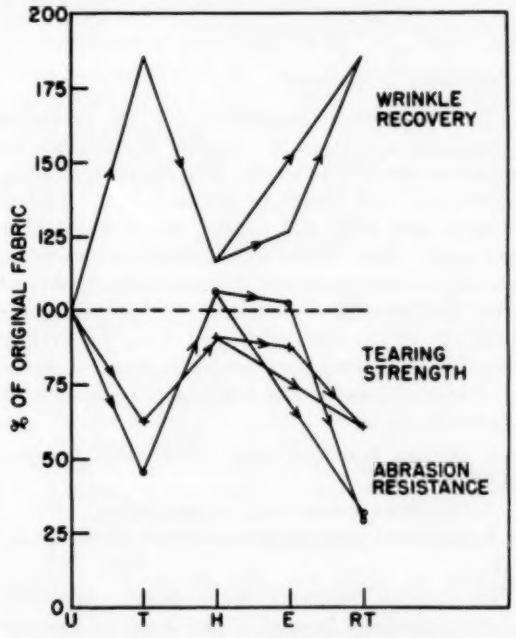

Fig. 2. Variations in textile properties of 80 × 80 cotton print cloth on application, removal, and re-application of resin treatment. Symbols are *U* untreated, *T* resin treated, *H* acid hydrolysed, *E* solvent extracted, *RT* re-treatment with resin.

its catalyst, cannot be given a satisfactory cure with a hand iron.

Thus, equally good results, with regard to wash and wear properties are obtained on (*a*) fabric treated directly, (*b*) fabric treated, hydrolyzed, and re-treated, (*c*) fabric treated, hydrolyzed, extracted, and re-treated, (*d*) fabric treated, hydrolyzed, and re-treated with CEU alone.

It is realized that this method of correcting errors in treatment may not be the answer in all situations. It is encouraging, however, that it is possible to re-treat the fabric after the nitrogenous resin is removed.

One disadvantage of the acid hydrolysis might be the effect on dyed and printed goods. In a brief experiment, samples of vat-dyed and pigment-printed print cloth were resin treated and then stripped by acid hydrolysis to remove the resin as before. The printed material was unaffected by the treatment or the hydrolysis. The color of the vat-dyed material was slightly deepened by the resin treatment and this color was unaffected by the stripping action. Therefore, it was concluded that this stripping method might be practical for some dyed and printed goods as well as for white goods.

Application to Garments

The remarkable permanence of the ironed-in creases was also noted in a number of miscellaneous garments which were treated with the resin solution, centrifuged, and ironed to dry and cure. Ladies' blouses, both plain and pleated, men's sport shirts and men's cotton slacks were treated with excellent results. Creases remained sharp and clearly defined after laundering up to six times. The garments were generally rinsed thoroughly and hung up to drip dry. By this means good wash and wear properties also were obtained. The following properties were observed:

1. Creases remained sharp after many launderings.
2. Garments needed little or no ironing.
3. Garments were wrinkle resistant during wearing.

In general, garments were neater, appearing freshly laundered because of the sharp creases and few wrinkles. In cotton trousers this was particularly noticeable. The cotton trousers were, by subjective evaluation, cooler and more comfortable to wear than before, because normally, the housewife would starch them to give a better appearance and more resistance to soiling.

Resin Finishing of Various Types of Cloth

It is well known that many factors influence the production of a satisfactory minimum care or wash and wear cotton fabric. These include weight and type of fabric, constructional factors such as yarn size and twist, fabric geometry, previous treatments, such as scouring or mercerizing, and even varietal differences in the cotton itself. In some cases the influence of these factors is not well understood. These same factors probably influence the permanent creases. Type of fabric seems to play an important part in the effectiveness of the treatment. In the present study a number of representative fabrics were treated with the standard CEU formulation. Drying and curing were conducted in one operation with a hand iron as before. Only a diagonal crease was pressed into these samples. In the fabrics treated, the only discernible factor of importance was the fabric weight. Heavier materials naturally require considerably longer curing times to effect a good cure. In Table V are listed physical data on a number of representative fabrics. The ironed-in creases were resistant to laundering and were not removed when ironed flat from the wet state after laundering. From these few results it would appear that the production of permanent creases is practical in many types of cotton garments.

Summary and Conclusions

In this short exploratory study of the possibility of application of resins to cotton to give permanent creases and shape-holding garments, it appears that a reactant-type resin, such as dimethylol cyclic ethylene urea, compounded with an acrylic thermoplast will give a satisfactory product. However, a number of disadvantages remain to be overcome. A more convenient process for custom application on a commercial scale must be developed. Reduction in the loss of strength and abrasion resistance would be highly desirable.

It was found that at least 4% add-on of resin was needed for good creases. Dimethylol cyclic ethylene urea resin from a number of commercial sources was used and all were found to be comparable. Best results were obtained when curing from the wet state; predrying was in some cases detrimental.

TABLE V. Treatment of Different Types of Cotton Fabric with the Standard CEU Formulation

Type of fabric	Tearing strength (warp), lb.		Breaking strength (warp), lb.		Flex abrasion (warp),* cycles		Wrinkle recovery angle (warp), deg.		Appearance of creases in treated samples
	Orig.	Tr.	Orig.	Tr.	Orig.	Tr.	Orig.	Tr.	
Sheeting, 5.2 oz. 60 × 45 (1.4% residual size)	9.7	2.8	78.1	51.3	2300	510	107	153	Excellent
Same, except 0.86% residual size	9.3	2.9	67.6	52.8	2300	370	100	146	Good
Same, except bleached, 0.33% residual size	9.0	2.6	82.3	54.7	490	430	92	152	Excellent
Sheeting, soft filled 40 × 43 3.2 oz.	4.0	1.9	21.5	17.1	71	11	102	150	Excellent
Sheeting, 5.2 oz. 48 × 48	4.8	2.5	56.8	36.4	960	140	95	151	Good
Lawn, 2 oz. 88 × 80, desized and bleached	1.4	0.8	31.5	17.4	260	21	80	155	Excellent
Organdy type, not starched, desized, boiled, scoured, and bleached, 1.3 oz.	1.6	0.8	25.7	10.7	140	6	107	160	Excellent
Osnaburg, 5.9 oz.	12.1	5.3	76.3	52.0	260	160	110	152	Good
Duck, 8 oz. bleached	15.7	6.1	120.2	78.4	3300	2100	97	150	Excellent
Twill, Khaki-dyed Army 8.2 oz.	4.8	5.3	129.4	117.0	2300	390	98	146	Excellent
Sateen, Marine green, 8.5 oz.	21.9	8.4	114.0	87.3	2000	110	121	155	Excellent

* Bar load 4 lb., head load 1 lb.

An ordinary electric hand iron gave excellent curing and crease-setting.

Lightly sized cotton accepted the treatment as well as desized material. Treated samples exhibited remarkable permanence of the finish, withstanding at least 12 simulated home launderings with excellent retention of creases. Samples suffered no discoloration or appreciable strength loss when subjected to the chlorine retention test.

It is possible to rectify errors made in the curing step by stripping the dimethylol cyclic ethylene urea from the cloth and re-applying. The other major component, an acrylate resin, may be removed by solvent extraction but this is unnecessary. When the thermosetting resin with catalyst is re-applied after stripping, the crease retention and wrinkle resistance of the treated cottons are as good as when treatment is with the original emulsion.

Application of the treatment to several types of cotton fabrics was made with excellent results. Ironed-in creases could not be removed by simulated home laundering.

Although the studies described here can be regarded only as preliminary, the treated cottons, with excellent characteristics of appearance, comfort, and wearability meet the requirements of modern informal living. It appears that with further research on resins and catalysts and with development of feasible commercial methods of resin application to cotton, garments able to compete with any synthetic fiber will be achieved.

Acknowledgments

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Flame Retardants for Cotton Using APO- and APS-THPC Resins

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Abstract

A new group of polymers made by reacting tris(1-aziridinyl)phosphine oxide, referred to as APO, or tris(1-aziridinyl)phosphine sulfide, referred to as APS, with tetrakis-(hydroxymethyl)phosphonium chloride, referred to as THPC, are good permanent-type flame retardants for cotton. All three of the compounds are water-soluble crystalline materials. The application of APO- or APS-THPC resins to textiles consists of padding fabric in an aqueous solution of the compounds, drying the fabric, curing it at about 140° C. for about 5 min. to polymerize the compounds, and then rinsing the fabric to remove any unpolymerized material.

About 8% of the resins in 8-oz. cotton twill or sateen is adequate to make the fabric pass the vertical flame test before or after 15 launderings with synthetic detergents, followed by an acid fluoride sour after each laundering. The flame resistance is also very durable to boiling alkaline soap solutions.

The properties of fabric treated with these new polymers are, in general, excellent. The hand and strength of the fabric is only slightly different from that of untreated fabric. The flame-resistant fabrics are resistant to rot and mildew.

SEVERAL permanent-type flame retardants for cotton have been developed at the Southern Regional Research Laboratory [2, 4, 5, 6, 8, 10]. Although it is believed that all of these represented improvements over those currently available for commercial use, none of our flame retardants are completely satisfactory. Because of the importance of this problem from a military and civilian point of view, our studies on flame-retardant finishes for cotton are being continued.

One of the flame retardants reported recently is based upon a THPC resin [8]. It is formed by the copolymerization of tetrakis(hydroxymethyl)phosphonium chloride, THPC, with a methylolmelamine and urea. It has received attention from a number of textile finishers and is now being used for finishing both cotton and viscose rayon. Finishing fabrics with the THPC resin is reasonably simple: it consists in padding fabric through an aqueous solution of the monomers, then drying and curing to polymerize the flame retardant inside the cotton fiber.

Two flame retardants which contain bromine have been reported by members of Southern Regional Research Laboratory. These are formed by making a telomer of triallylphosphate and bromoform in one case [4] and a telomer of allylphosphonitrilate and bromoform in the other case [5]. The polymers are prepared in aqueous emulsion. They are applied to fabric in essentially the same manner as THPC resins.

Two additional flame retardants were reported that are formed by combining about one part of either of the aqueous emulsions of the telomers with about three parts of THPC resin-forming monomers [6, 10]. The resulting emulsions are also applied to fabric by the same technique used to apply the THPC resin.

The purpose of the present paper is to present our most recent and interesting flame retardants which are based upon resins made by reacting THPC with aziridinyl compounds. These compounds are tris-(1-aziridinyl)phosphine oxide, $(\overline{CH_2CH_2N})_3P=O$, which we refer to as APO and tris(1-aziridinyl)-phosphine sulfide, $(\overline{CH_2CH_2N})_3P=S$, which we refer to as APS. These aziridinyl compounds may also be named NN'N" triethylenephosphoramide and NN'N" triethylenethiophosphoramide respectively. These APO-THPC and APS-THPC flame retardants are not mere modifications of THPC-amine resins and are not a combination of two existing flame retardants. Instead, they are new thermosetting resins.

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APO and APS are prepared by reacting ethylenimine with $POCl_3$ and $PSCl_3$, respectively. The reaction may be represented as follows:

$$POCl_3 + 3HN\overline{CH_2CH_2} + 3R_3N \rightarrow$$

$$OP(N\overline{CH_2CH_2})_3 + 3R_3N \cdot HCl$$

It is carried out by adding the oxy- or thiochloride to a cold solution of ethylenimine and an acid acceptor like triethylamine in some inert solvent such as benzene [1]. Then the amine hydrochloride is filtered off, and the organic solvent is distilled. The residue consists mainly of the crude aziridinyl compound which can be purified by crystallization from benzene. APO and APS have been prepared several times and the yields have averaged about 90%. APO melts at 41° C. and APS at 51° C. Both compounds are soluble in water and a number of organic solvents. These compounds have been studied recently as agents for retarding cancer growth. Both compounds were found to be useful in this respect [3, 7].

APO and APS react with THPC to form highly flame-resistant thermosetting resins. Aqueous solutions of APO or APS and THPC are stable for many hours at about 25° C., but when heated to about 100° C. or higher, reaction and subsequent resinification occur rapidly. The initial reaction of APO with THPC may be indicated as shown here.

$$OP(N\overline{CH_2CH_2})_3$$

$$+ (HOCH_2)_4PCl \xrightarrow{[O]} (\overline{CH_2CH_2N})_2P(=O)NCH_2CH_2 \cdot$$

$$|$$
$$H$$

$$- O - CH_2P(=O)(CH_2OH)_2 + HCl + HCHO$$

Note that the phosphonium structure shown in THPC has been converted to a phosphine oxide structure. It is indicated in this manner because it has been found that THPC is converted to tris-(hydroxymethyl)phosphine oxide by heat, either in alkaline or acid conditions. With respect to the addition reaction, one of the aziridinyl rings was opened by one of the methylol groups of THPC to form a stable ether-type bond. In the initial reaction product there still exists two aziridinyl rings and two methylol groups which may also react. Therefore, extensive reaction leads to highly cross-linked polymers. And to add further to the complexity of the reaction, the hydrogen atom attached to the nitrogen as a result of ring opening is reactive toward both aziridinyl rings and methylol groups.

Fortunately the textile finisher does not have to be too much concerned with the various reactions. For him the reaction is simple. He merely impregnates fabric with an aqueous solution of the reagents, dries it at a relatively low temperature, and then cures it at about 140° C. to produce the flame-resistant polymer in the fabric.

Experimental

Preliminary experimentation indicated that useful flame retardants might be made by polymerizing APO or APS with THPC in cotton fibers. But the preferred mole ratio of monomers, the amount of resin, and the curing temperature had to be established.

Influence of Mole Ratio of APS to THPC upon Resin Add-On and Tear Strength

According to theoretical considerations APS and THPC should form highly cross-linked polymers over a rather broad mole ratio range. This is no doubt the case under drastic conditions. Since it is preferred to process cotton under just as mild conditions as possible, the amounts of these reagents should be selected so that as much of the compounds can be polymerized in cotton as possible under mild conditions. In order to establish the preferred amount of the reagents, aqueous solutions made up to contain various mole ratios of the reagents were used to treat an 8-oz. sateen under a selected set of conditions. In each case, the solution contained some APS, THPC and an amount of triethanolamine equivalent to one quarter of the weight of THPC used. The primary purpose of the triethanolamine was to neutralize free hydrochloric acid which is usually present in THPC. The combined weight of APS and THPC in each solution amounted to 20% of the total solution. The composition of the solutions used is shown in Table I.

Samples of 8-oz. sateen were padded through various solutions using a tight nip so that the wet pickup was 53% (± 1%). The samples were dried 4 min. at 80° to 90° C. and cured 5 min. at 140° C., then washed 30 min. in hot tap water containing a detergent, rinsed, and dried. The increase in weight of the resin-treated fabrics is termed resin add-on.

It is shown in Table I that the resin add-on was

TABLE I. The Influence of Mole Ratio of APS to THPC upon Resin Add-On and Tear Strength

Treating solution					Resin add-on	Tear strength, Elmendorf, lb.	
THPC		APS		TEA,*			
%	Moles	%	Moles	%	%	W	F
16.0	4	4.0	1	4.0	2.3	6.3	5.4
15.0	3	5.0	1	3.7	2.9	7.3	5.6
13.3	2	6.7	1	3.3	4.4	8.5	9.2
10.0	1	10.0	1	2.5	6.7	10.1	12.5
6.7	1	13.3	2	1.7	7.2	10.3	—
5.0	1	15.0	3	1.2	6.2	10.2	—
4.0	1	16.0	4	1.0	6.6	9.8	—

* TEA = triethanolamine.

low in each case where the mole ratio of APS to THPC was less than 1:1. That is, the add-on increased as the concentration of THPC in the treating solutions decreased until a maximum was reached at about 1 mole of APS per mole of THPC. The mole ratio of APS to THPC had a similar influence upon the Elmendorf tear strength; the tear strength reached a maximum and leveled off when the molar concentration of APS was at least equal to that of THPC. Therefore, for the greatest efficiency of resin formation and best tear strength, under the limiting conditions of this experiment, the APS should be present in at least a 1:1 molar ratio to THPC.

Influence of Cure Temperature upon Resin Add-On and Tear Strength

Experiments were run in which two 8-oz. fabrics of different construction were padded with aqueous resin-forming solutions, dried 4 min. at 85° C., and then cured 5 min. at various temperatures. In these experiments APS-THPC and APO-THPC solutions were used as the resin-forming solutions. In both cases the concentration (by weight) of the aziridinyl compound was equal to the THPC concentration (this is about a 1:1 molar ratio). The total concentration of aziridinyl compound plus THPC was 33 and 25%, respectively, for APS-THPC and APO-THPC solutions. The APS-THPC solutions were used to treat 8-oz. sateen and APO-THPC solutions were used to treat 8-oz. twill. The wet pickup of the fabrics was 60% (± 1%) for the sateen and 57% (± 1%) for the twill. It can be seen in Table II that the resin add-on increased as the curing temperature increased, but the tear strength decreased as cure temperature increased. It is intresting to see that the tear strength of the treated twill is substantially better than untreated control fabric even at the 140° C. cure temperature, whereas the sateen retained essentially all of its original tear strength up to only 130° C. cure. According to these data, the preferred curing temperature would be dependent upon whether a good tear strength or good efficiency of reagents was desired. A good compromise might be 135° C.

Minimum Amount of Resin Needed in 8 Oz. Fabric

A number of samples of 8-oz. twill treated with APO-THPC resin were examined to determine the minimum amount of flame retardant needed in these materials as measured by the Vertical Flame Test. The fabrics were all treated with solutions containing an equal weight of THPC and aziridinyl compound. The amount of resin put into the fabric samples was varied by altering the concentration of resin-forming reagents in the treating solutions. Flame resistance was determined by the vertical flame test [11]. The test was made on fabrics that contained as little as 3.6% resin. It is shown in Table III that 8-oz. fabrics containing 6.8% resin passed the flame test before an alkaline boil. About 10.2% or more was needed for the fabric to pass the flame test after a 3-hr. boil in a solution containing ½% soap and 0.2% sodium carbonate.

A sample of 8-oz. sateen containing 7.8% resin was given 15 launderings according to Federal Specifications [11], method 5556, using Igepon T * as the detergent and an acid fluoride sour following washing. This sample passed the Vertical Flame Test after the 15 washes. Therefore it appears that

TABLE II. Influence of Cure Temperature upon Resin Add-On and Tear Strength

Cure temp., °C	Resin add-on, %		Tear strength, lb. Elmendorf (w)	
	APO-THPC on twill	APS-THPC on sateen	APO-THPC on twill*	APS-THPC on sateen†
110	6.7	6.7	8.1	13.0
120	8.8	10.5	7.2	10.2
130	10.2	11.1	7.0	11.6
140	11.3	11.9	5.4	8.0
150	11.6	—	4.0	—

* Tear strength of untreated twill was 4.9 lb.
† Tear strength of untreated sateen was 11.9 lb.

* Mention of trade names is for information and convenience only and does not imply their endorsement over materials not mentioned.

TABLE III. Minimum Amount of APO-THPC Resin Needed in 8-Oz. Cotton Twill

Resin add-on, %	Flame resistance, char length	
	Original, in.	After 3-hr. alkaline boil, in.
5.6	BEL*	BEL
6.5	BEL; 4.4	BEL
6.8	4.5	BEL
8.0	4.4	BEL
8.8	4.2	BEL
10.0	3.6	BEL; 4.3
10.2	4.0	4.6
11.2	4.4	5.1
11.6	4.3	4.4

* BEL means that both of the test samples burned the entire length of the strip.

about 8% resin is adequate in fabric to be laundered with neutral detergents, whereas slightly more than 10% is needed if the goods are to be given strongly alkaline washes.

Flame Retardancy of APO- and APS-THPC Resins on Other Fibers

A qualitative experiment was run in which APO- and APS-THPC resins were put on a number of fabrics, some consisting of hydrophobic fibers, some of hydrophilic, and one consisting of a blend of the two types of fibers. In most cases a rather high resin add-on was obtained. The flame resistance was determined by the Strip Flame Test [9]. That is, the angle was determined at which a 1-cm. strip of the fabric failed to support combustion when held at the angle indicated and ignited at the end with a match or other source of flame. The treated fabrics fell into two categories. They were either highly flame-resistant or had no flame resistance. It is clearly shown in Table IV that the resins do not contribute flame resistance to the hydrophobic fibers which are orlon, nylon, or acetate rayon, but do make viscose rayon, fortisan, and cotton flame resistant. The blended fabric which contained about 75% cotton with 25% nylon was also made flame-resistant.

Processing of Fabric

There are additional details that still need to be studied before the best method of applying APO- and APS-THPC resin to fabric will be known. Therefore, we have tentatively adopted a very simple procedure for processing based upon experimental data and experience with other resin finishes. The procedure presented below describes a typical run on pilot plant equipment.

Procedure

A treating solution was made by dissolving 350 g. THPC, 87 g. triethanolamine, 350 g. APS, and 20 g. Triton X-100* in 1193 g. water in the order given. The temperature of the solution was 30°–35° C. and pH was 6.1. The concentration of the resin-forming constituents, THPC plus APS, was 35%. Fourteen yards of half-width 8-oz. sateen were padded through the solution using two dips and two nips. The wet pickup was 65%. The wet fabric was immediately dried 4 min. at 85° C. and then cured 5 min. at 140° C. Salts and unused reagents were removed by a jig wash consisting of a cold rinse, a hot wash using 0.01% Igepon T,* a hot rinse, and a cold rinse using 5 ends in each step. After drying on a tenter, the fabric was softened by padding it through a 3% solution of Triton X-400* to a 50% wet pickup and drying again. The fabric contained 16% resin.

A piece of fabric containing 10.5% of the APS-THPC resin was made by using the procedure, as described above, except that the aqueous treating solution contained 12.5% THPC, 12.5% APS, 3.1% triethanolamine, and 1% Triton X-100.*

TABLE IV. Flame Retardancy of APO- and APS-THPC Resins on Other Fibers

Fabric description	Resin used	Resin add-on, %	Flame resistance, angle
Viscose rayon	APO-THPC	27	180
	APS-THPC	12	170
Orlon	APO-THPC	34	0
	APS-THPC	25	0
Nylon	APO-THPC	29	0
	APS-THPC	21	0
Acetate rayon	APO-THPC	12	0
	APS-THPC	10	0
Fortisan	APO-THPC	26	180
	APS-THPC	11	135
Cotton	APO-THPC	22	180
	APS-THPC	15	180
Cotton-Fortisan	APO-THPC	20	180
	APS-THPC	17	170
Cotton-Nylon	APO-THPC	25	180
	APS-THPC	17	135

Fabric Properties

A number of small samples of 8-oz. twill and sateen have been processed essentially according to the procedure given just above. Most of the earlier samples were tested only for flame resistance, durability, and tear strength. The most recent samples, shown in Table V, were examined more thoroughly. Therefore, emphasis has been placed upon test data from these samples, although some of the earlier samples had somewhat better tear strength.

Test data is given in Table V for 8-oz. twill and sateen treated with APO-THPC and APS-THPC resins, and for twill treated with APO-APS-THPC resin. The last fabric was obtained by treating twill with an aqueous solution containing 8.5% APO, 8.5% APS, 17% THPC, 4% triethanolamine, and 1% Triton X-100.*

Durability

A sample of sateen treated with APS-THPC resin and containing 1.55% nitrogen and 1.45% phosphorus was soxhlet extracted 3 hr. with tetrachloroethylene. The flame resistance was unchanged by the extraction. After extraction the fabric contained 1.54% nitrogen and 1.50% phosphorus.

A sample of 8-oz. twill containing 14.1% APS-THPC resin with 1.51% nitrogen and 1.47% phosphorus was boiled 3 hr. in a 0.5% soap solution containing 0.2% sodium carbonate. Analyses after the boil gave 1.3% nitrogen and 1.25% phosphorus. The char length of the boiled sample was 3.5 in. as compared with 4.0 in. before the boil.

The resins are also very resistant to laundering techniques described in Federal Specifications [11]. Table V shows that an 8-oz. fabric containing as little as 7.8% APO-THPC resin passed the Vertical Flame Test after 15 of the launderings. None of the fabrics described in Table V passed the Strip Flame Test after the 15 laundry cycles, but another sample (8-oz. sateen) containing 14.9% APS-THPC resin did pass the Strip Flame Test after the fifteenth laundering.

Strength

The strip breaking strength might be reduced but only slightly. Considering the values reported in Table V under strip breaking strength, four samples of sateen lost an average of 6% tensile strength. However, if one considers the strength values recorded under chlorine retention for untreated con-

TABLE V. Properties of Resin-Treated Twill and Sateen

Test	8-Oz. sateen					8-Oz. twill			
Resin and add-on, %	Untreated control	APS-THPC 14.3	APO-THPC 15.0	APS-THPC 10.2	APO-THPC 7.8	Untreated control	APS-THPC 15.7	APO-APS-THPC 14.3	APO-THPC 15.5
Strip breaking strength (w) lb.	115	112	108	108	109	134	126	116	123
Abrasion resistance									
1. Flex (w)	1578	749	728	819	1149	2498	891	1084	772
2. Flat	525	779	650	593	—	—	—	—	—
Elmendorf tear (w) lb.									
1. Original	A.C.*	10.0	8.2	11.0	11.4	10.7	5.7	6.6	6.4
2. After 15 washes	11.2	8.0	8.3	8.8	7.8	—	—	—	—
Stiffness (bending moment × 10^4 in. lb.)	10	12	12	11	9	16	26	16	21
Char length (in.)									
1. Original	—	3.0	2.8	3.6	2.8	—	3.1	2.9	2.7
2. After 5 washes	—	2.5	2.7	4.1	3.7	—	—	—	—
3. After 15 washes	—	3.2	3.6	4.6	6.1	—	—	—	—
Chlorine retention strength (lb.) after									
1. Wash (no bleach)	113	114	112	—	—	—	—	—	—
2. Wash with bleach	114	113	117	112	—	—	115	111	118
3. Wash with bleach and scorched	110	107	110	111	—	—	112	116	119

* A.C. = above capacity of machine which is about 13 to 14 lb.

trol and two samples of resin-treated sateen, the strength loss would be nil. But on the other hand, the resin-treated 8-oz. twill does show an average loss in strength of 9%.

The two most difficult objectives in the development of permanent-type flame retardants for cotton fabric are the maintenance of good hand and tear strength. In our present work, the Elmendorf tear test has been used to evaluate tear strength retention. These new resins do reduce tear strength but not as much as is usually obtained with other known permanent-type flame retardants. It seems that the strength retained should be adequate for most uses.

Samples of twill shown in Table II retained 100% tear strength. It appears from Table V that the tear strength decreases as the amount of resin put into the fabric increases. However, this decrease is only slight.

Hand

The hand of fabric treated with APO- and APS-THPC resins is altered only slightly. It feels a little fuller and is slightly springy due to a mild degree of crease resistance. Since the resin goes inside the fibers, the feel is still essentially that of untreated cotton. One factor influencing the hand is stiffness. The stiffness of several fabrics is shown in Table V. The differences in stiffness values for the untreated and treated sateen are all within experimental error. The differences in stiffness for the twill are slightly more than experimental error.

Abrasion Resistance

Two test methods have been used to determine abrasion resistance. It is doubtful if either method actually reflects use tests. According to the flex abrasion method, as shown in Table V, the resin treatments reduce abrasion resistance substantially, but according to the flat abrasion tests, the resin actually improves the abrasion resistance.

Chlorine Retention

Chlorine retention has been a fault of many resins used on cotton. In order for a flame retardant to be generally useful, it should be resistant to chlorine bleach. This is another property in which APO- and APS-THPC resin-treated fabrics are very satisfactory. It is somewhat unusual for a nitrogenous resin to be unaffected by chlorine bleach. According to Table V, the resin-treated fabrics did not lose strength when they were washed with a solution containing a chlorine bleach and then ironed. White sheeting treated with the resins were discolored somewhat by the chlorine bleach.

Rot Resistance

Another plus feature of these resin-treated fabrics is resistance to rot. For many uses, flame-resistant fabrics are given an additional processing to impart rot resistance. With APO- and APS-THPC resin-treated fabrics, the rot resistance is "built in." The amount of rot resistance obtained with these resins has not been fully established, but it has been determined in one soil burial experiment that 88% strength was retained after 25 days and 65% after 38 days in a rot bed where untreated control fabric lost essentially all of its tensile strength within 10 days.

Discussion

The experiments reported here are preliminary and have served to select a good set of processing conditions but are not necessarily the best. Additional experiments are being run to establish conditions which will produce flame-resistant fabrics with the best properties possible.

The pH of the resin-forming solutions used to prepare the fabrics described herein has been about 6.0. Just how the pH affects the resin-forming solutions is not fully known. It is known, however, that alkaline solutions cause the conversion of THPC to tris(hydroxymethyl)phosphine oxide which reacts with the aziridinyl compounds more slowly than THPC. Also at low pH values, the resin-forming solutions are less stable than at about 6.

A very important factor in the use of these new flame retardants is the stability of the resin-forming solutions. Some APO- and APS-THPC resin-forming solutions have been prepared and used immediately and then set aside at about 10°–15° C. for 24 hr. and then used again. There was a slight change in hand and tear strength due to aging of the solutions. The fabrics treated with the aged solutions were slightly stiffer and the tear strengths were about 25% less. Therefore, it appears that the solutions could be made up and used for 8 hr. without producing noticably adverse effects. It should be understood that heat should not be used in dissolving the reagents, nor should the resin-forming solutions be heated before or during use.

A flame-retardant finish satisfactory for military and civilian use must withstand the laundering tech-

niques used by these groups. For example, for military use it must withstand washing with a neutral detergent and a fluoride sour. For industrial use, it must withstand strong alkali washes. Household laundering is usually less severe than either of these. In many cases the finish must also withstand chlorine bleach. According to the data obtained, fabric finished with APO- and APS-THPC resins should be satisfactory for all these uses.

It should be emphasized that the amount of these resins needed in 8-oz. cotton fabric (about 8%) to make it pass the Vertical Flame Test after 15 launderings is substantially less than that of any other known durable flame retardant. The only other flame retardant approaching this efficiency is the retardant made by combining one part of a telomer of bromoform and allylphosphonitrilate with three parts of THPC resin [6].

Substantially more of the APO- and APS-THPC resins are needed (about 15% for 8-oz. twill and sateen) in a fabric for it to pass the Strip Flame Test.

The cost of the new flame retardants is prohibitive considering the present price of ethylenimine which is used in making APO and APS. The cost of ethylenimine is probably largely due to the small-scale production of the compound because the process for making it is simple and the reagents used in the process are cheap. Phosphorylchloride is a cheap chemical and thiophosphoryl chloride should sell for about the same price if produced in large quantities.

Up to now we do not know which of the aziridinyl compounds is most suitable for use in a flame-retardant finish. However APS is more stable than APO when stored.

Summary

New flame retardants based upon resins made by reacting APO and APS with THPC have been developed. Fabrics are treated by padding them through an aqueous solution of either APO and THPC or APS and THPC, then drying and curing at an elevated temperature to form the insoluble resin inside the fibers.

The new flame retardants have the following outstanding features:

1. The treating solutions show good stability.
2. The amount of resin needed in a fabric is very low in comparison with other durable flame retardants.
3. The resin treatment alters the hand of fabric only slightly.
4. The tear and tensile strengths of treated fabric are good.
5. The strength of treated fabrics is not damaged by chlorine bleach.
6. The resin is very resistant to neutral and alkaline washes.

Acknowledgment

The authors wish to thank Dr. Ruby K. Worner and Mrs. Janice M. Evans for the textile evaluation tests and Paul J. Murphy and Julian J. Jurgens for the phosphorus and nitrogen analyses, respectively.

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The Application of Wrinkle-Resistant Finishes to Cotton Garments

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Abstract

The practical application of a conventional crease-proofing formulation to cotton garments is described.

WITHIN the last five years, the application of crease-resistant finishes to cotton has become of major and increasing interest in the industry. The improved appearance, wearability, and ease of care of the resin-treated fabrics have met with general consumer acceptance. However, many cotton garments that are not crease resistant are still being marketed. Some garment manufacturers have not chosen to use treated fabrics because of the extra cost, manufacturing difficulties, such as needle cutting on some constructions and resistance to pressing, and some fear reduced serviceability from loss of strength associated with resin treatment. Although we do not necessarily agree that these deficiencies are critical, the treatment of the finished garment does overcome the manufacturing difficulties while achieving the benefits of resin treatment.

In the past the non-mill application of resin presented a critical problem; suitable curing apparatus is not found outside of plants set up for resin finishing. The success of the work reported here is based on the development of a resin/catalyst system that cures rapidly, when dry, on heating to a temperature only slightly above the boiling point of water. Curing under ironing or pressing conditions then becomes feasible. Although curing must be rapid at the temperatures established on pressing or ironing, it is essential that little or no curing should take place on simple drying; should curing take place in a wrinkled condition, satisfactory ironing would then be impossible.

The formulation we chose to study consisted of the following commercially available components:

	% solids
1. *Thermosetting resin* of the methylol cyclic urea type	7.0
2. *Curing catalyst* of the metal-salt type	0.5
3. *Thermoplastic emulsion polymer* of the acrylate type	1.4
4. *Hand builder* of the polyvinyl-alcohol type	0.5
5. *Fiber lubricant* of the silicone type	0.5

In all crease-resistant finishes, the thermosetting resin (such as a urea-formaldehyde, cyclic urea-formaldehyde, or melamine-formaldehyde type) with a curing catalyst, is the essential ingredient. The other components were introduced either to improve the hand of the garment and/or to improve the so-called wash and wear properties. As discussed by Abrams [1] and Steele and Brown [4], soft thermoplastics provide a significant improvement in crease recovery without introducing further significant

Fig. 1. Percale print cloth skirt. Treated, washed, drip-dried, and worn one day.

losses in strength. A hand builder was introduced since a crisp hand now seems to be associated by the consumer with crease-resistant finishes. Lubrication of the fibers by a silicone improves hand, ease of ironing, and tear strength. None of the above additives is truly unique, but each has been found from experience to approach an optimum. Many other materials of a similar nature could be substituted with varying degrees of success.

The rapid curing properties of the above formulation are illustrated by the data of Table I. Rapid curing properties of the resin/catalyst system are further illustrated by the data of Table II, confirming the previously recognized slow curing of melamine resins relative to the cyclic urea type. Urea/formaldehyde resins were not considered for this work because of poor storage and bath stability, greater danger of damage on bleaching, inherently low crease-proofing efficiency, and danger of fish odor.

In practice the garment is immersed and squeezed several times in the above formulation, centrifuged

TABLE I. Crease Recovery versus Curing Temperature

(Crease-Proofing Formulation on 80² Cotton)

Cure (min./°F.)	Crease recovery °(W+F/2)
Air-dried	106
1/220	131
1/240	133
1/260	141
Silicone and acrylic only	86

TABLE II. Crease Recovery versus Thermosetting Resin Type

(Crease-Proofing Formulations on 80² Cotton)

Resin type	Metal cat.	Crease recovery °(W+F/2)
Cyclic urea	Zn^{++}	133
	Mg^{++}	129
Melamine*	Zn^{++}	(incompatible)
	Mg^{++}	109

* 50% more melamine used than cyclic urea.

Fig. 2a. Broadcloth sport shirt. Untreated, washed, and drip-dried.

Fig. 2b. Broadcloth sport shirt. Treated, washed, and drip-dried.

or spun to remove excess liquid, shaken out, and hung to dry partially in as wrinkle-free a condition as convenient. Ironing can be carried out with a steam or dry iron, with the garment either damp or dry. Ironing while damp with a steam iron is the most desirable set of conditions from the standpoint of ease. As illustrated by the data of Table I, some curing does, indeed, take place on simple drying. Complete curing is ensured by a final dry ironing at the wool setting, about 375° F. Applications have also been carried out by commercially accepted drycleaning processes at the National Institute of Drycleaning.

Although applications have been carried out successfully in the laboratory and in the home, several shortcomings were encountered.

1. In both the drying and ironing operation, considerable formaldehyde is evolved. Many people would find this objectionable.

2. The initial ironing must be done with more than usual care. Depending on garment construction, the ironing operation can be quite tedious. An advantage as well as a deficiency of the treatment is that any crease ironed in cannot be removed without stripping out the resin.

3. No all garments or all fabrics respond with equal satisfaction. Garments having puckered seams, multilayered waist bands, cuffs, shoulder pads, etc. can yield permanent puckers and creases.

4. Fabric limitations are the same as for any crease-resistant finish. Loosely woven fabrics with large loosely twisted yarns, in symmetrical weaves, yield the best results. Oxford cloth and 80² percale represent favorable examples in contrast to twills.

5. Some dyes are reported to exhibit shade changes on resin treatment. We have noticed this with only one garment, but the possibility should be considered.

6. Caution must be exercised in application of crease-resistant finishes to old garments. Common to all resin treatments is loss in tear, tensile, and abrasion resistance. If a garment has become tender with wearing and washing, a crease-resistant finish may well weaken it to an unserviceable level. Obviously, if a garment was designed to be used close to the limits of the fabric strength, such as work denims, a resin finish would not be advisable.

In general the above-described treatment has been found most satisfactory on women's blouses, skirts, and dresses, and men's sport shirts. (See Figures 1 and 2.) Some of the treated garments have exhibited excellent wash and wear properties.[1] Those that have not been entirely satisfactory require only the lightest ironing. Somewhat less satisfactory have been cotton slacks of which we have examined only denims and twills. Although of the same twill weave, the denims, having a looser weave of larger yarns, exhibited the better wash and wear properties. Construction at the waist and cuffs also contributed to the problems of application of the crease-resistant finish (see Figure 3).

Probably of as great or greater interest than the wash and wear properties of the treated garments is their greatly improved wearability. Several of the treated skirts, for example, instead of requiring pressing after each wearing could be worn repeatedly without pressing until soiled. The appearance during wearing is also considerably enhanced (see Figure 1).

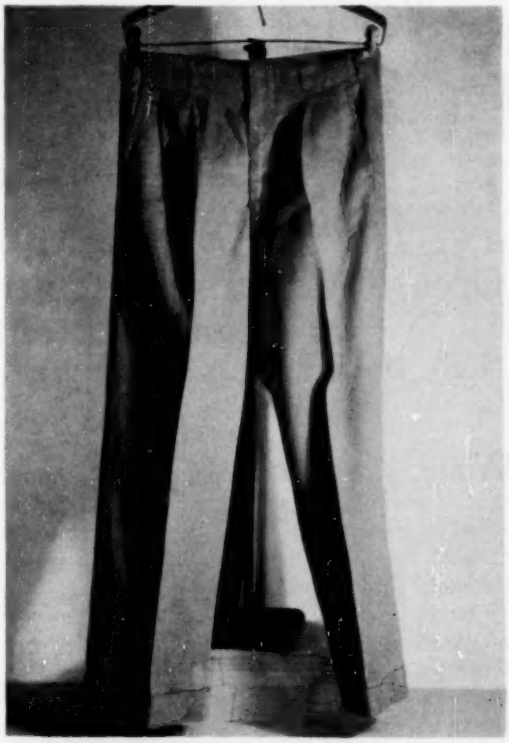

Fig. 3. Sport denim slacks. Treated, washed, and drip-dried.

[1] Wash and wear properties were used as a criterion, since they represent the ultimate in crease-resistant finishes.

While the obvious applications to finished garments, such as described above, are of considerable interest, there are other applications of greater novelty. Recently there have appeared on the market excellent sport jackets of resin-treated cotton. Since these are finished with rolled sleeves, there is no problem of pressing in creases. However, it has not been possible to manufacture slacks of the same high quality of tailoring; it is most difficult to introduce a sharp crease into a crease-resistant fabric. There is now the possibility of sending out the slacks in an untreated condition, and then having the slacks treated after cuffing by some independent processor, such as a dry cleaner, who is set up for the work. Admittedly this would be a complicated arrangement. A simpler arrangement might result if the garment manufacturer would treat the finished garments; those creases put in later when the garment is cuffed would not be as sharp as those of the leg creases, but the wearing properties at the cuff edges would be improved.

The application of a crease-resistant finish to a garment makes possible custom pleating not only by the manufacturer but also by the women who sew at home. It is also within the realm of possibility that fabric could be marketed in a treated, uncured condition. After cutting and sewing, curing could be accomplished on simple pressing or ironing of the finished garment. This latter scheme has not yet been reduced to practice since the systems we have examined will either give slow curing when simply dried on the fabric, or will not cure at all.

The above discussion has been qualitative in nature, since we have merely described a new technique in the well-known field of the resin treatment of cotton [2, 3]. It is hoped that this novel development will expand the market for textile chemicals as well as for cotton.

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The Application of Crease-Holding, Wrinkle-Resistant Treatments to Cotton Garments by Drycleaners

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WHEN we first became aware of the potential value of developing a technique for imparting improved crease recovery properties to finished cotton garments, we felt that the drycleaner was in a unique position to perform this service.

First of all the drycleaner can supply the skill and experience in the finishing or pressing of garments that is so important here. Second, he is already equipped in most plants with the machinery and equipment that can be used to apply the resin finish and cure it on certain types of cotton clothing. And last, the process may provide the cleaner with an additional service to offer during the summer months, when the normal cleaning volume declines.

During the past several weeks, we have applied a crease-resistant resin finish to 35–40 different types of cotton garments, using the equipment in our commercial drycleaning plant. These tests are to be considered preliminary, practical trial runs, since we have not yet made any attempt to determine the effect of certain variables in connection with the various steps in the operation.

We shall first outline the operations followed in our plant runs and then give a brief description of the drycleaning equipment which was used.

1. The resin bath was made up in a water bath as follows:

12% of a thermosetting resin of the cyclic urea reactant type.
5% of a thermoplastic resin based on acrylic-type materials.
2% silicone emulsion. One purpose of this ingredient is to prevent sticking of the thermoplastic resin during the ironing and pressing operation.
1.25% of a metal-salt-type catalyst.
0.1% of a nonionic surface-active agent.

2. Immerse the garments in the treating bath at room temperature until they are thoroughly wet out.

3. Extract garments in an extractor until they have about 70% wet pickup.

4. Dry the garments with hot air (120–130° F.). Both the rotary tumbler and the wind-whip have been used for this operation.

5. Cure the resin by pressing the garment on the hot-head press and/or with a hand iron.

6. Wash the garments in a detergent-water bath, followed by thorough rinse.

7. Extract lightly.

8. Dry using tumble dryer, wind-whip or cabinet dryer.

The drycleaning equipment used in this work is usually found in most plants and consisted of the following items:

1. *Immersion Tubs*

This type of tub or some other suitable container is found in the wetcleaning portion of a plant. The resin bath is made up in here and the clothes are immersed for the first step.

2. *Extractor,* 18-in. diameter

This is the familiar centrifugal extractor for removing the excess liquid from the clothes.

3. *Tumble Dryer*

The damp clothes are tumbled dry in the perforated cylinder which rotates inside the steel cylinder. Heated air is passed through the load and out the exit stack. In this operation, it is important not to let the air temperature become so high that it commences to polymerize the resin in the clothes.

4. *Wind-Whip*

This drying equipment provides a current of air blowing vertically upward through the garment. The air can also be heated, if desired, by passing it over steam coils before it contacts the garment. This type of drying operation is required for certain garments that might lose shape too much if tumble-dried. It also has the advantage that the ballooning action of the moving air tends to remove wrinkles in the wet fabric (see Figure 1).

5. *Hot-Head Press*

The bottom of the press is stationary and padded to make a firm support for the garment. The top, or head of the press, consists of a smooth metal surface. Steam at about 70- to 80-lb. gauge pressure circulates inside this head so that the surface temperature on the metal is in the order of 300° F. To operate the press, the head of the press is lowered, and it may be held or locked against the garment for any length of time desired.

6. *Hand Iron*

This iron is heated by electricity and it can be set at various settings (rayon, silk, wool, cotton, etc.) similar to many home irons. Certain portions of a garment (collars, sleeves, etc.) are best finished or pressed with the hand iron. For the pressing of an entire garment, therefore, both the hot-head press and the hand iron may be used.

Fig. 1. Wind-whip.

7. Rotary Washer

On some of the garments we processed, the wash given after heat-curing the resins was carried out in the familiar type of rotary washer (shown in Figure 2). Certain other garments, because of their construction, were washed by hand.

In processing these items of clothing, we have been favorably impressed by the crease recovery properties that have been imparted to the fabric in many instances. Results were especially effective on medium-weight cotton sport shirts, cotton dresses, skirts, and blouses. As would be expected, we found in general the process showed up to better advantage on garments containing printed or woven designs than it did on fabric dyed a solid shade. Also, on several of these medium-weight dresses and blouses, the process improves the durability of pleated areas or other desired creases in the garment.

Not unexpectedly, we found some garments that did not respond as well as others to our preliminary trials. Several pairs of heavy cotton twill trousers were not rendered as crease resistant as we would like. Also the creases in the trouser legs were not very durable after a washing operation. We feel that such factors as fabric weight and fabric construction were responsible in part at least for the less satisfactory showing of these trousers. It is very probable, too, that modifications in our method of curing the resin can produce some improvement here.

In spite of our limited successes on cotton trousers at first, we felt that crease-resistant cotton trousers with a durable crease down the leg would have considerable appeal. The National Cotton Council, in fact, suggested that a man's entire suit be made up of cotton and be processed to give a wrinkle-resistant finish and durable creases in the trousers. The suit has actually been made up, the wrinkle-resistant resin was applied and cured in our plant and the suit has been worn by one of the men in the National Cotton Council group.

The processing of this suit was naturally more difficult during the curing and pressing operations than would be the processing of a shirt or dress. Nevertheless, it was possible to produce a marked improvement in the crease resistance and the durability in the trouser crease in this cotton fabric.

We have deliberately avoided applying these resins to white garments which would possibly be exposed later on to chlorine bleaching. One of the resins used here is susceptible to chlorine retention and the familiar hazards that accompany it.

Almost any new process or new application of a process brings certain questions to light or uncovers certain problems that must be solved. The present instance is no exception, and there are several areas of further study that appear important. To date, we have tried only one resin formulation. Other proportions of urea resin and acrylic resin or other types of catalyst may possibly work more advantageously in this application. The effect of various time intervals for curing the resin (using the hot-head press or hand iron) on various weights of fabric is another unknown at present.

In the pressing operation, an occasional unwanted wrinkle may be put in the garment. Normally, the presser can merely steam the area to remove the wrinkle. In a resin-treated garment the wrinkle will not come out that easily. Techniques for removing this type of defect will need to be worked out.

Both the hot-head press and the steam iron are equipped so that dry steam under pressure can be applied directly to the fabric. The idea has been

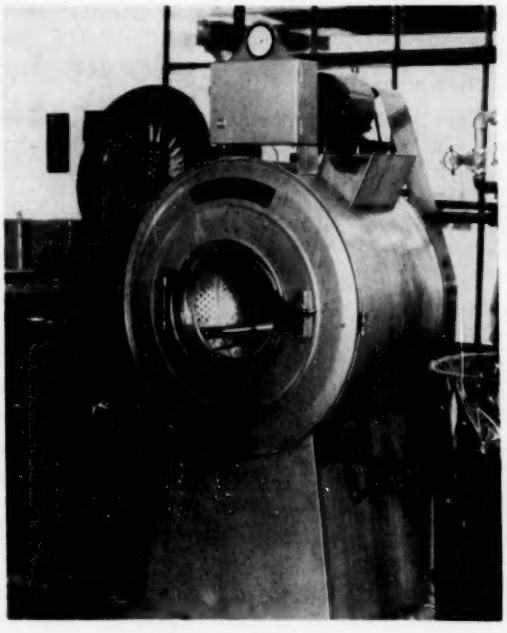

Fig. 2. Rotary washer.

suggested so that this source of heat could possibly be used for curing the resin, although we have done no work on this technique to date.

The questions just indicated are not a complete list, but they do provide some idea of our thinking on this subject.

Our trial runs have demonstrated that it is possible for a drycleaner to apply wrinkle-resistant or crease-holding finishes to cotton garments using equipment available in the plant plus the operator's skill and experience in finishing and pressing these garments. Some problems and questions have arisen, but all of them appear capable of solutions and answers if sufficient study is given to them.

Book Reviews

Organic Chemistry. 3d Ed. Louis F. Fieser and Mary Fieser, New York, Reinhold Publishing Corp.; London, Chapman & Hall, Ltd., 1956. 1112 pages. Price $10.00.

Reviewed by Ludwig Rebenfeld, Textile Research Institute, Princeton, N.J.

This reviewer considers himself fortunate that the first edition (1944) of Fieser and Fieser, "Organic Chemistry" was available when he began his study of this ever-expanding branch of chemistry. The new third edition of Fieser and Fieser is a welcome addition to the broad literature in this field and represents a distinct contribution to the methods of presenting the facts and theories of organic chemistry.

The book strikes an excellent balance between three distinct phases of organic chemistry: general reactions of organic compounds, including methods of synthesis and structure determination of the several classes of organic compounds; theories of organic chemistry, including stereochemistry, ring formation and stability, conformational analysis, orbital theory, resonance theory and reaction mechanisms; and finally, discussions both from the theoretical and practical points of view of definite types of compounds such as fats, proteins, polymers, dyes, carbohydrates, and many others.

An extremely useful feature of this edition is not only the inclusion of problems at the end of every chapter, but also the presentation of answers to these problems at the end of the book. Brief biographical sketches of eminent chemists mentioned in the text are presented as footnotes. Both these features make the book valuable and interesting from a student's point of view. While this book is not intended to replace the elementary texts of organic chemistry, it should be considerably useful to beginning students as a handy reference book for additional reading on selected topics. The book will be equally useful to the advanced student as a general all-inclusive textbook of organic chemistry. The industrial chemist will also wish to have this book available in order that he may become aware of the advances in the over-all field of organic chemistry through this integrated presentation.

One of the finest features of the past two editions has been the extensive and complete index which enabled the reader to locate a particular topic with little effort. It is gratifying that this extensive index is again available in the third edition; a separate author index has been added.

Textile Machinery Index. Oldham, England, John Worrall, Ltd., 1956. 644 pages. Price £2-2-0 postpaid.

This is a new addition to Worrall's textile directories and publications. It provides full information on the activities of British firms engaged in the manufacture of textile machinery, accessories, chemicals, and associated equipment. It was compiled in collaboration with the Textile Machinery and Accessory Manufacturers' Association.

The Index is arranged in three sections. Section 1 (466 pages) furnishes general information about manufacturers and suppliers of textile machinery, power plant and power transmission equipment, accessories, mill supplies, and services. Section 2, "Buyer's Guide," contains an alphabetical listing of firms in Section 1. Section 3 gives general information about firms in the field of textile chemicals. In addition to the list of products and activities, branch offices in Great Britain and overseas are given. The system of indexing provides easy access to the information in the book.

The Chemistry and Technology of Waxes. 2d ed. Albin H. Warth, Reinhold Publishing Corp., New York, 1956. 940 pages. Price $18.00.

Reviewed by Hillary Robinette, Jr., Robinette Research Laboratories, Inc., Ardmore, Pa.

The author, Dr. Albin H. Warth, has presented in this second edition of "The Chemistry and Technology of Waxes" truly, in the words of the publisher, a "Wax Bible." Every chemical compound having waxlike properties appears to be mentioned in this work. The term "wax" is used in its broadest sense to cover all waxlike solids and liquids found in nature, irrespective of their source or method of preparation.

The volume is divided into ten chapters, each chapter supplying a generous amount of information related to the particular chapter heading. The first chapter discusses the chemical components of waxes, the second chapter, the natural waxes—animal, vegetable, insect, and microorganism. The fourth chapter deals with fossil waxes, the fifth with petroleum waxes, the sixth with synthetic waxes, the seventh with blended and compounded waxes, the eighth with emulsifiable waxes, the ninth with analytical methods used in the identification and the utilization of waxes, and the tenth with the use in industry of the various waxes. Each chapter contains numerous references to the original literature, and these listings are to be found at the end of the chapter. In a number of instances, specific processing details are included, and specific formulations for use and application are also to be found. The volume contains an author index and an excellent subject index.

"The Chemistry and Technology of Waxes" is recommended to all of those who have need to know of the origin, the constitution, or the utilization of waxlike substances. It is an ideal reference source, bringing together information which could not be readily found without extensive library searching. The author is to be commended on the preparation of this up-to-date edition.

The Chemistry of Phenolic Resins. Robert W. Martin, John Wiley and Sons, Inc., New York, 1956. 298 pages. Price $9.50.

Reviewed by Hillary Robinette, Jr., Robinette Research Laboratories, Inc., Ardmore, Pa.

"The Chemistry of Phenolic Resins" is an excellent, orderly survey of the chemistry, both practical and theoretical, of the reactions and reaction mechanisms involved in the formation of phenolic resins. Mr. Martin, an expert in the field of resin chemistry, adequately discusses the major types of reactions of phenols with aldehydes and ketones, insofar as resin formation is concerned. In addition, consideration is given to nonresinous products resulting from the reaction of phenol with aldehydes and ketones.

The volume is divided into ten chapters covering the various reactions involved and has an adequately prepared index. Numerous tables showing structure and physical characteristics of the more important products are included. Throughout the volume structural formulas are used profusely to assist in communicating to the reader the theory and practice so well delineated. Many pertinent references are included at the end of each chapter.

The volume is recommended to all of those interested in the chemistry of phenolic substances and their reaction products leading to resin formation by leading to pure compounds having utility as organic chemical raw materials.

Dictionary of Textile Terms (German-English, English-German). M. Polanyi, London and New York, Pergamon Press, 1956. 328 pages. Price 60*s*. or $11.00.

This pocket-size German-English, English-German dictionary comprises the most widely used terms in the various textile industries and allied branches. It is a handy reference for all persons in any way connected with the many ramifications of the textile industry, whether in manufacturing, technology, or distribution.